VOLUME XIII SECOND SERIES NUMBER 6

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THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

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PUBLISHED BY
THE AMERICAN PHYSICAL SOCIETY
LANCASTER, PA., AND ITHACA, N. Y.

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THE PHYSICAL REVIEW, ITHACA, N. Y.

Second Series *June, 1919* *Vol. XIII., No. 6*

THE

PHYSICAL REVIEW.

THE FUNCTION OF PHASE DIFFERENCE IN THE BINAURAL LOCATION OF PURE TONES.

By R. V. L. Hartley.

Synopsis.—This paper offers an explanation of the sound images observed when pure tones of the same frequency and intensity but of different phase are applied to the two ears. Use is made of theoretical curves calculated by Stewart and Fry giving the relation between the position of an actual source and the resulting phase difference P of the sound at the two ears. On the assumption that the listener subconsciously perceives the phase difference and places the image in the position that experience has taught him to associate with that phase difference, most of the observed phenomena follow directly from the curves.

For frequencies below about 600 cycles they account for (1) the observed rotation of the image with continuously varying P; (2) its motion toward the ear followed by a range of uncertainty as P approaches 180°; (3) the increase with frequency of the value of P for maximum lateral displacement of the image. For higher frequencies they explain the progressive decrease in definiteness of the image with increase in frequency as due to the presence of a number of simultaneous images. These multiple images as given by the curves are in very good agreement with those observed in the rather unique experiments of Bowlker.

The completeness with which the assumed theory of direct perception of phase difference explains the observed phenomena is strong evidence in its favor against the rival theories based on cross conduction through the head.

Introduction.

THE problem of the location of a source emitting a pure tone presents features which differentiate it quite sharply from the general problem of sound location. In the first place, pure tones are much less easily localized than are complex sounds. And in the second place, persons who are deaf in one ear have almost no sense of location for pure tones (provided the head is fixed), even though they may locate other sounds almost as well as a person with normal hearing.

Hence, while both monaural and binaural effects may be utilized in locating complex sounds, the location of a pure tone is essentially binaural, and so must depend upon differences in the characteristics of

the sound reaching the two ears. A sustained pure tone is completely determined by its frequency, amplitude and phase, and of these characteristics only the last two are subject to variation with the position of the source. It follows therefore that the sense of location can be dependent only on differences of intensity or phase or both. The existence of a connection between relative intensity and location was probably recognized before that of phase difference, but both have been known for a comparatively long time. In what follows it will be assumed that the effect of relative intensity is reduced to a minimum by keeping the intensities equal at the two ears.

Stewart,[1] in his article on Binaural Beats, includes a very good review of the literature on phase difference as affecting location. The experimental results may be very briefly summarized here. Two general methods have been used. In one, a particular phase difference is maintained by means of an adjustable difference between the paths from a single source to the two ears. In the other the phase difference is made to vary continuously by exciting the two ears from sources of slightly different frequency. The rate of variation is determined by the difference in frequency.

It is commonly observed that with zero phase difference, the apparent source of the sound, or for brevity the image, is in the median plane. Its location varies with different experimenters but more often appears to be in front. For frequencies below about 600 cycles it is agreed that the image lies on the side for which the phase at that ear leads. With continuously varying phase difference the image is described as starting from a position straight in front for zero phase difference, moving more or less in a circle to one side, till opposite the ear, then moving in toward the ear, entering the head, jumping quickly to the other ear for 180°, and continuing on around to the front along a similar path on that side. For higher frequencies most observers report a falling off in the definiteness of the location and finally a complete loss of the sense of direction.

In attempting to explain the mechanism by which the phase difference determines the position of the image, two general theories have been advanced. One of these, which we may term the direct perception theory, assumes that the listener is able to take cognizance of a difference in phase, as such, and by virtue of his past experience, or that of his ancestors, is able to associate any particular phase difference with the direction from which he has been accustomed to receive sounds having that phase difference.

[1] G. W. Stewart, PHYS. REV., June, 1917, p. 502.

Lord Rayleigh[1] has attempted to explain in a general way the observed facts on the basis of this theory. He pointed out that for a fork of 128 cycles, moving around the head, the phase difference would never exceed about one eighth of a period, and commented on the fact that in the laboratory experiment the location effect persisted for phase differences right up to half a period. He noted also that at a frequency around 512, the phase difference with the source opposite one ear should be 180° and concluded there could be no discrimination at that frequency for sounds directly right or left. For somewhat higher frequencies he pointed out that the same phase difference could be produced by a sound on either the right or the left, and considered it fortunate that our sense of direction fails us at the point where it would begin to give misleading results. It should be noted that in arriving at the phase difference for an actual source at one side he made use of the very rough assumption that the difference in the paths to the two ears is one foot. He also drew other conclusions from the unjustifiable assumption that the sense of lateralness is a maximum when the phase difference is 90°. On the whole, his results were not particularly conclusive.

Against this theory certain psychologists advanced the argument that it involved a violation of the general principle that the sensation resulting from the stimulation of a sensory nerve is independent of the nature of the stimulus. In other words, they held that the characteristic phase of the sound stimulus at each ear could not be preserved in the nervous impulses reaching the brain as would be necessary for a perception of difference in phase. Apparently, however, this general principle, has been deduced from rather limited experimental evidence, and it is not considered by psychologists generally to be very definitely established. This objection, therefore, is not sufficient to warrant a rejection of the theory, provided it can be shown to be satisfactory in other respects.

Nevertheless, it was probably this argument which led to attempts on the part of physicists to show how differences in phase could give rise to differences in the intensity of the stimuli, which latter would cause a location on the side of the stronger stimulus. This resulted in various theories being advanced which we may designate as cross-conduction theories, since they are based on the assumption that an appreciable fraction of the sound entering each ear is conducted through the head to the other ear and there combines with that entering directly.

Myers and Wilson[2] present such a theory. In order to make the directions fit the experiments they find it necessary to introduce an

[1] Rayleigh, Phil. Mag., 13, 1907, pp. 214 and 316.

[2] C. S. Myers and H. A. Wilson, Proc. Roy. Soc., 80, 1908, p. 260.

arbitrary phase reversal in passing through the head. Even then their theory explains only the most general features of the experiments, since it makes the displacement of the image proportional to the sine of the phase difference. More recently Stewart[1] has embodied the same idea in a more elaborate theory and uses it to account for the location when the phase difference is between 90° and 270°. For the rest of the cycle he assumes direct perception of phase.

Against this type of theory numerous objections have been raised. Probably the most important of these is the experimental evidence showing that the amount of sound actually reaching the ear by cross-conduction is far too small to produce the effects ascribed to it. A good summary of this evidence is given by Peterson.[2] Further, if the location effect due to phase difference were determined purely by the resulting intensity relation it should be very strongly affected by changes in the relative intensity of the sounds coming to the two ears. Under certain conditions, however, it is found to be practically unaffected by very considerable changes of this sort. In order to give even a qualitative explanation of the phenomena it is necessary to introduce a purely arbitrary assumption of phase reversal within the head. To make the agreement at all quantitative even over a limited range of frequency, it has been necessary to set up a very complicated theory involving a rather large number of assumptions.

To put the situation briefly then, the cross-conduction theory, while it does give something of an explanation, is open to very serious objections. The direct perception theory, on the other hand, while it has nothing very serious against it, has so far had no very positive evidence advanced in its favor, such as would be furnished by a quantitative explanation of the experimental facts. The most obvious line of attack then is to find out whether or not any such explanation is possible on the basis of direct perception.

PURPOSE.

It is the present purpose to attack this question by attempting to trace a correlation between the phase differences produced at the ears by actual sources in various positions and the positions of the images which result when sounds of equal intensity and predetermined phase differences are applied experimentally to the two ears.

DATA AND DISCUSSION.

For this the first essential is a knowledge of the phase at the ear as a function of the position of the source for various frequencies. Stokes[3]

[1] G. W. Stewart, PHYS. REV., June, 1917, p. 514.

[2] Joseph Peterson, Psychol. Rev., Vol. 23, No. 5, p. 333, 1916.

[3] Lord Rayleigh, Theory of Sound, Ch. 17.

has developed a method whereby it is possible to calculate, for any point on a great circle of a rigid sphere, the phase of a sound whose source is in the plane of the great circle. The wave-length of the sound and the distance of the source are expressed in terms of the radius of the sphere. Stewart[1] has applied this method to the calculation of certain special cases. At the time this work was undertaken, T. C. Fry, a colleague in the Western Electric Co., had, independently, applied the method to certain other cases. A study of these two sets of results led to the conclusions described below. Later Fry extended his calculations securing the results from which have been plotted the curves given in Figs. 1 to 5.

Stewart assumes the head to be such a rigid sphere of 60 cm. circumference, the ears being at opposite ends of a diameter. For a single case, corresponding to a source, of frequency about 280 cycles, distant about 480 cm., he plots the difference in phase at the two ears as a function of the direction of the source. The only deduction which he draws from this curve is that, "The phase difference changes the most rapidly when the source of sound is in front or behind the hearer."

In plotting the curves of Figs. 1 to 5, the circumference of the head was assumed to be 55 cm. (radius, $r = 8.75$ cm.). The angular separation of the ears in the horizontal plane was taken as 165° and the velocity of sound as 340 m. per second. The figures represent progressively increasing frequencies. The individual curves of each figure are for sources at various distances R from the center of the head, ranging from $2r$ to infinity. (Unfortunately, the method of calculation was not adaptable to sources at the surface of the head where $R = r$.) Abscissæ represent the angular displacement ϕ of the source from a point straight in front, being taken positive to the right and negative to the left, 180° being at the back. Ordinates represent the phase lead P at the right ear over the left. Negative values then mean that the phase is leading at the left ear. A phase lead $180° + x$ ($x < 180°$) at one ear is equivalent to a lead of $180 - x$ at the other ear. In other words, those parts of the curve where the phase lead exceeds 180° in either direction must have 360° either added or subtracted so as to keep the ordinates between $-180°$ and $+180°$. This has been done in Figs. 3, 4 and 5.

From this theoretical information it is possible to predict, on the basis of the direct perception theory, where a listener should place the image when the phase difference at the ears is given any arbitrary value. For it is only necessary to read from the curve corresponding to the frequency of the sound, the value of ϕ corresponding to the given value of P.

[1] G. W. Stewart, PHYS. REV., 1914, 4, p. 252.

As the curves give only those values of ϕ lying between $-90°$ and $+90°$, they give only the images located in front of the observer. If extended to $\phi = 180°$ in each direction the curves would be nearly symmetrical with respect to $\phi = \pm 90°$. (The departure from symmetry is due to taking the ears as 165° apart rather than 180°.) This means that any particular phase difference could be produced by a source either in front of or behind the observer and hence we should expect the image to be in either one or both of these positions. As already noted some experimenters find it in one place and some in the other. Inasmuch as the

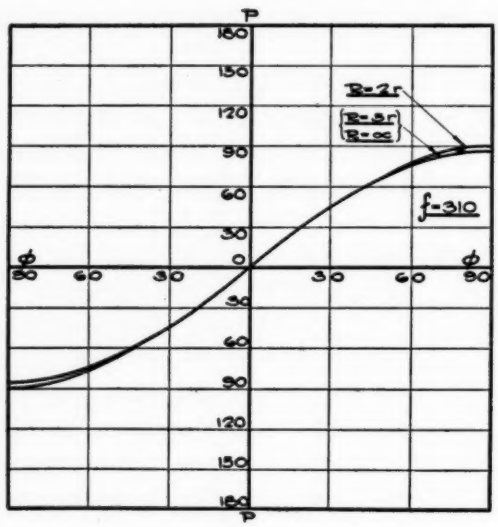

Fig. 1.

majority seems to find the image in front, the discussion will be limited to those quadrants with the understanding that the same general conclusions hold for images at the back.

Consider first the case of the low frequency note of 310 cycles, shown in Fig. 1. For values of phase difference less than about 86°, we may for each ordinate choose an abscissa lying on any one of an infinite number of curves distributed between those of $R = r$ and $R = \infty$. This means that so far as phase alone is concerned there is in this region nothing to fix the distance of the image, while its angular position is determined, within limits, by this distance. The observed fact that the image is generally at a considerable distance is probably to be explained by the equality of intensity. Generally speaking, for any given direction the intensities at the ears become more nearly equal the greater the distance of the source. This then would explain why the image in moving around from the front would stay at a considerable distance till it was

opposite the ear for a phase difference of 86°. For a further increase in phase there is no longer a corresponding abscissa on the curve for $R = \infty$ so it is necessary to go to the curve for the greatest distance which will still give a point. This means that once the image has reached a position near 90° its direction remains unchanged, but in spite of equal intensity, it moves in toward the ear, reaching it for a phase difference somewhat greater than 90°, being the maximum value of the hypothetical curve for $R = r$. This is in agreement with the observations quoted above for the case of continuously changing phase difference. Beyond this point there is no corresponding position for an actual source and hence the curves tell us nothing as to where an image is to be expected. However, it does not follow that such phase differences are foreign to the experience of the listener. They may very easily be produced by the reflections which occur in an enclosed space. Or they may occur when the source is within the head, or when the latter is in direct contact with the sounding body. Most observers describe the image as being located within the head in this case. Bowlker,[1] however, speaks of the image as being spread over a considerable angle on either side of 90°. In any case the definiteness of the sense of location should be much less than for small phase differences. It is, therefore, not surprising that, as Stewart has observed, the position of the image is affected much more by unequal intensities when the phase difference is near 180° than when it is near zero.

Consider next the effect of increasing the frequency. Up to something over 600 cycles (Figs. 1 and 2) the curves are of the same general form and we should expect the same general behavior of the image, as is found to be the case. The main variation is that the phase difference at which the image reaches its maximum lateral displacement increases with the frequency. Thus for 620 cycles (Fig. 2) the sense of lateralness should be a maximum for about 170°, instead of 90° as Rayleigh assumed. In support of this variation in the value of P for maximum image displacement, may be cited the results obtained by Myers and Wilson[2] using a variable path arrangement. They give curves in which the sensation of lateralness, measured in arbitrary units, is plotted against the path difference, and attempt to show a connection between this apparent displacement and the sine of the phase difference. An inspection of the curves, however, shows that for a frequency of 128, the maximum displacement occurs for a phase difference considerably less than 90°, while above 90° the displacement shows a decided falling off. At 384 cycles, the maximum is more nearly at 90°, while for 512, it is

[1] T. J. Bowlker, Phil. Mag. (6), 15, p. 318, 1908.

[2] C. S. Myers and H. A. Wilson, *loc. cit.*

on the side toward 180°. What is perhaps a more striking confirmation is a statement made by Bowlker,[1] in connection with some experiments in which various path differences were obtained by placing tubes of different lengths over the two ears and listening to a distant sound. He says "A wave-length of about 36 inches (frequency about 370) . . . gave an image displaced 90°. Sound with longer wave-length gave a dis-

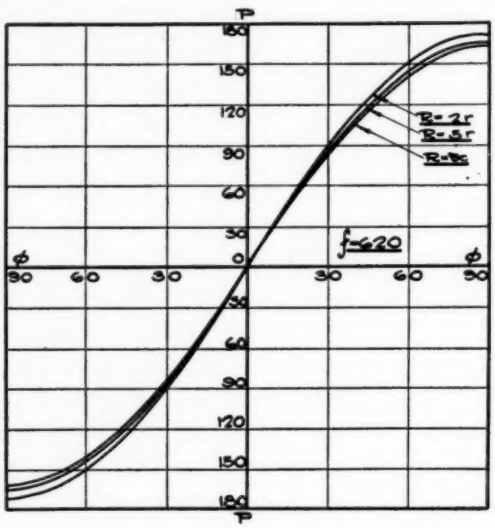

Fig. 2.

placement of 90° before a phase-difference of half a wave-length was reached, and the sound image then seemed to spread over a continually increasing length of arc on each side of 90°."

As the frequency is still further increased a marked change occurs in the nature of the curves owing to the fact that an actual source may then cause a phase difference greater than 180°. For a frequency of 930 cycles, Fig. 3 shows that for ordinates above 126° there are, on the curve for $R = \infty$, two abscissæ, one positive and one negative. This means two images, one on the right and one on the left. In the range between 126° and 106° there can be no image at infinity on the left, but there can be one at some distance greater than $2r$. (As before, the equality in intensity should tend to keep the image as far away from the head as is consistent with the phase relations.) For P less than the critical value corresponding to $R = r$, there is only one image as at lower frequencies.

Starting then with $P = 0$, the image is in front. As P increases the image moves rather slowly to the right keeping at a considerable distance.

[1] Bowlker, *loc. cit.*

When P is somewhat less than 106° it has moved out about 20°, when a second image appears at the left ear. This new image moves quite rapidly outward from the ear, reaching a great distance by the time the first has moved to 33° (P = 126°). It then swings around in a circle toward the front, at first rather rapidly and then more slowly, arriving at 51° on the left at the same time that the other image reaches the same position on the right (P = 180°). To complete the cycle P must be varied from − 180 to 0°. The image on the right now moves on around the circle with increasing speed till opposite the ear, when it moves in to the ear and disappears. Meanwhile, the left image moves slowly toward

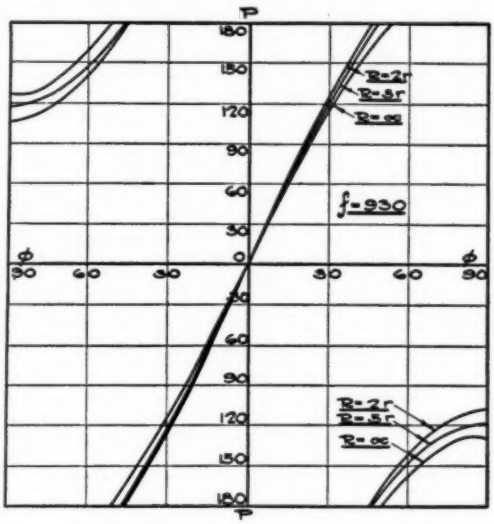

Fig. 3.

the front reaching there for P = 0. That is to say, the two images follow the same path relative to their respective sides but in opposite directions. The one on the side where the phase-lead is increasing begins in front and disappears at the ear, the one on the other doing the reverse. It will be noticed that the paths followed are exactly the same as for the low frequencies discussed above. The difference lies in the magnitude of the variation of P required to cover the path.

For still higher frequencies the range on either side of 180° in which two images are present increases progressively (see Fig. 4) until the whole cycle is covered. For higher frequencies still, where the possible phase difference exceeds 360°, there should be a third image for values of P close to zero, being on the right for small positive values of P and on the left for negative. Fig. 5 shows a case where this third image is present for most of the cycle. For still further increasing frequencies it follows

from the above that the greatest number of images in the field during any part of a cycle increases by one each time the maximum possible phase difference increases by 180°.

Before the foregoing picture of the sound images for high frequencies can be used to predict the experimental results to be obtained at those frequencies, there must be something known or assumed as to the ability of the listener to perceive and localize a plurality of simultaneous images, giving to each the location assigned to it by the phase relations. It is quite conceivable that the listener would be unable to do this, in which

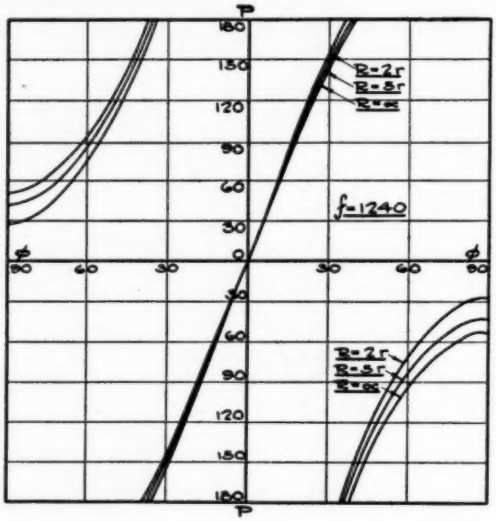

Fig. 4.

case he might either have the sensation of a single image in some sort of average position or he might have no sense of direction at all. In either case his judgment would be much less certain than for a single image. Under these circumstances he would probably be influenced considerably by the equality of intensity, which would tend to cause him to locate the image in the median plane, particularly since at high frequencies the variation of intensity ratio with the position of the source is more marked than at low. This assumption appears to be in agreement with the results of most observers, who find that from about 600 cycles upward the sense of location by phase difference becomes progressively less trustworthy. That the change should appear to be gradual follows from the fact that the region of two images is at first confined to a small part of the cycle and gradually extends over the remainder. So far then, the theoretical deductions are not inconsistent with the experiments, on the assumption that more than one image can not be located separately.

That this is not universally true, however, is shown by a series of experiments by Bowlker,[1] in which he was able to recognize two and even three separate images, in the field at once. Whether this was due to some peculiarity of his apparatus or of his individual sense of hearing is not known, but in either case the experiments are of special interest as being probably the only ones available for testing the above theory regarding multiple images.

The method used was an improvement of that referred to above in which tubes of unequal length were used. In order to eliminate possible

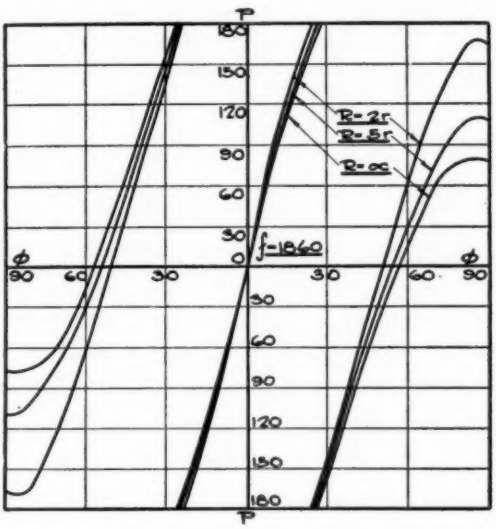

Fig. 5.

inequalities of intensity due to the unequal lengths of the tubes, or to sound shadows cast by the head, he used exactly similar tubes on the two ears, bending them upward so as to make the openings horizontal in a plane well above the top of the head. The difference in path was then secured by facing in various directions relative to the source. The latter consisted of an organ pipe about 30 feet away. The distance L between the openings was 31 inches. The path difference was given by L into the sine of the angle turned through from the position facing the source. With this arrangement he was able to locate the direction of the sound image with considerable exactness, especially near the front. Due to some asymmetry either of the tubes or the ears, the image, when facing the source, was not always exactly in front. It was necessary for some frequencies to turn through as much as 4° to bring it in front. This position was then used as the corrected zero. At moderately low

[1] Bowlker, *loc. cit.*

frequencies the image moved around toward the side of leading phase, until at a point corresponding to a path difference of half a wave-length ($P = 180°$), it jumped to a similar position on the left. Continuing the rotation till this new image was straight in front the angle was generally found to agree quite closely with a path difference of a whole wave-length. The position of the image just before and after it crosses to the other side he calls the crossover angle. At frequencies of 263 and 335 he gives this as "90° (wide image)," which agrees with his results for unequal tubes. At higher frequencies it decreases progressively, having the following values; for 485 cycles, 40° to 50°; 690 cycles, 36°; 970 cycles, 18°, and 1290 cycles, 15°. He speaks of this cross-over angle as being "near the maximum displacement that phase will produce with the particular wave-length under observation."

At this point he reduced the separation of the openings to 15 inches so as to avoid the necessity of measuring very small angles. Repeating the experiment with 1,290 cycles he found for the cross-over-angle, 20°. He also observed that for all positions corresponding to phase differences between 180° and about 100° both images were present in the field at once. At 1,675 cycles he says: "Two images were evident during nearly the whole range—there were practically always two and sometimes three images evident, though I had some doubts whether the central image was always real or a result of attention to the two side images." In place of the cross-over angle he gives the maximum displacement as 12°.

He then reduced the apertures of the tubes from 2 inches to 0.6 inches. For a note of 2,090 cycles he says, "now three images could always apparently be heard together when facing one of them." The maximum displacement is here given as about 9°. At 2,310 cycles, "the image further to the left seemed stronger and tended to draw off one's attention." At 3,050 cycles, "it was very difficult to determine even approximately the position of an image, the one to the left of the two or three in the field of view seeming the loudest as a rule. I only felt sure that phase was still playing a part in fixing the maxima and minima which gave rise to the centers of the sound images."

The general agreement of these experiments with the theoretical results is obvious. The order of the changes in the images with increasing frequency is in striking agreement. First at low frequencies there is the progressive increase in the value of P to give maximum lateral displacement, accompanied by a narrowing of the region in which the image appears diffuse. This represents the range of frequency in which the maximum of the $P - \phi$ curve is less than 180°. Next comes a range in which the displacement of the image for $P = 180°$ is less than 90° and

decreases progressively with increasing frequency. This corresponds to the diminishing value of ϕ for $P = 180°$, over the frequency range in which the values of maximum phase difference exceed 180°. Along with this comes the appearance of a second image on the opposite side, the part of the cycle for which it is present increasing progressively. When it has covered the whole cycle a third image appears, corresponding to the condition where the maximum value of P exceeds 360°.

The quantitative agreement is, however, not exact. The greatest angular displacement in the case of multiple images is always given as quite small and never reaches 90° as the theory would indicate. Also the frequencies at which the additional images appear are rather higher than the theoretical values. The second of these discrepancies is probably a result of the first. Suppose, for example, that in Fig. 4 the observer could not detect the second image when its displacement exceeded say 45°. The second image ($R = \infty$) would then appear when P reached 170° instead of 50° as it otherwise would. In order to have it appear at 50° under the assumed conditions it would be necessary to go to a higher frequency. That the second image should not have been detected under certain conditions is not surprising, when it is considered that practically all the other experimenters have failed to observe it at all. Furthermore, the assumptions underlying the theoretical calculations are such that we should not expect a very close agreement with experiment. The head is not a sphere nor is its circumference likely to be exactly 55 cm. The ears do not lie on a great circle and in most cases are not separated by exactly 165°. In fact, the differences, both physical and psychological, among the different observers are so great that there should be wide variations in the experimental results themselves. It should be strongly emphasized, therefore, that although fairly definite quantitative values have been given, it has been done chiefly for the sake of clearness in exposition, and there is no justification for using these values to predict with equal definiteness the results of any given experiment.

RESEARCH LABORATORY OF THE
WESTERN ELECTRIC COMPANY, INC.

AN EXTENSION OF THE ELECTRON THEORY OF METALS. I. THERMOELECTRICITY AND METALLIC CONDUCTION.

BY A. E. CASWELL.

SYNOPSIS.—Using as a starting-point the simple equations deduced from the electron theory by J. J. Thomson and others for thermo E.M.F., thermoelectric power, Peltier E.M.F. and the Thomson effect, and assuming that the number of free electrons in unit volume of a metal is an exponential function of the temperature, the author shows that (1) the thermoelectric power is a linear function of the temperature, (2) the equations relating thermo E.M.F. and temperature, and Peltier E.M.F. and temperature, represent parabolas having their axes perpendicular to the axis of temperature, and (3) the Thomson effect is different for different metals and may be either positive or negative, but will usually have a positive temperature coefficient. Likewise, using the equations for electrical and thermal conductivity and making the second assumption that the number of positive centers with which the electrons collide changes with the temperature (these centers being atoms, molecules or clusters of molecules), it is found that (4) the electrical conductivity of pure metals decreases with increase of temperature but is not exactly inversely proportional to the absolute temperature, (5) the peculiar behavior of the electrical resistance of alloys can be accounted for, and (6) the thermal conductivity may either increase or decrease with the temperature, the temperature coefficient depending both upon the temperature and the material. A third assumption, viz., that the positive centers take part in the conduction of heat but not of electricity, leads to the conclusion that (7) the usual value deduced for the Wiedemann-Franz-Lorenz ratio is too small, and the variations in the value of this ratio at ordinary temperatures is accounted for. The above theoretical results, especially (1), (2) and (3), are, at least within the ordinary range of temperatures, in substantial agreement with experiment, since the constants involved in the theory can be determined from experimental data, and so the author concludes that (8) the concentration of electrons in a metal is an exponential function of the temperature, and (9) the number of positive centers changes with the temperature, the exact relation being somewhat uncertain. The number, however, must generally increase with the temperature.

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1. INTRODUCTION.

THE theory outlined in this paper is an attempt to amplify, or expand, the electron theory of metals as applied to thermoelectricity and metallic conduction so as to bring it more nearly into harmony with the experimental facts without at the same time doing violence to such portions of the theory as are not treated here. Three simple assumptions, relating the electrons, molecules and temperature, are made which will be studied in detail later. Certain mathematical forms are employed to express the assumed relations. It is not claimed that these expressions are more than first approximations to the true functions, neither is it claimed that they are even first approximations in the neighborhood of the absolute zero and temperatures near which marked changes in the structure of the material occur. It is claimed, however, that the theory presented here offers, at least within the range of ordinary temperatures, as good an explanation of the experimental facts here treated as previous theories do, and it explains some facts which have been unaccounted for hitherto.

At the outset the writer wishes to state that much of such merit as the present paper possesses is due to the fact that he has had the advantage of constant consultation with his colleague, Professor W. P. Boynton, whose familiarity with the kinetic theory of matter has made his numerous suggestions and criticisms of primary importance.

Throughout this discussion the symbols employed have the following meanings:

m = mass of an electron,
u = "mean square velocity" of the electrons,
T = absolute temperature,
t = Centigrade temperature,
α = the gas constant for a single electron, being defined by the equation $\frac{1}{2}mu^2 = \alpha T$,
ϵ = charge on an electron,
λ = mean free path of the electrons,
N = number of free electrons in one c.c. of a metal,
n = number of positive centers in one c.c. of a metal,
P = Peltier E.M.F.,
Q = thermoelectric power,
E = thermo E.M.F.,
σ = Thomson E.M.F., or so-called "specific heat of electricity,"
κ = electrical conductivity,
ρ = electrical resistivity, and
k = thermal conductivity.

The other symbols used are constants whose significance is obvious from the context. The subscripts 1 and 2 are used to refer to two different metals except where some other convention is specifically stated.

A theory to be completely satisfactory should account for the following facts.

1. The thermo E.M.F. between any two metals can usually be expressed by an equation of the form $E = At + \frac{1}{2}Bt^2$.

2. Similarly, the thermoelectric power of any two metals can usually be represented by a equation of the form $Q = A + Bt$.

3. The Peltier E.M.F. must satisfy the equation $P = QT$.

4. The Thomson effect may be either positive or negative and is different for different metals.

5. The Thomson effect has a temperature coefficient.

6. The electrical conductivity of pure metals at ordinary temperatures is almost inversely proportional to the absolute temperature, or the resistivity is nearly proportional to the absolute temperature. Usually the resistivity increases somewhat more rapidly than the absolute temperature.

7. At ordinary temperatures the electrical conductivity of alloys is frequently nearly independent of the temperature and occasionally increases with increase of temperature.

8. The thermal conductivity of a number of metals is nearly constant at ordinary temperatures and may either increase or decrease as the temperature is raised.

9. The ratio of the thermal to the electrical conductivity at all ordinary temperatures is nearly the same for all metals, the ratio being nearly proportional to the absolute temperature. In the case of pure metals the ratio usually increases somewhat faster than the absolute temperature, but in the case of alloys it usually increases more slowly.

Besides the facts just enumerated which are explained in the present paper there are number of galvanomagnetic, thermomagnetic and electronic emission phenomena which must ultimately be explained. No attempt is made to account for these effects, their treatment being reserved for a subsequent paper. So far as known none of the hypotheses advanced here in any way interferes with the explanation of any of these effects.[1]

[1] For general discussions of the above phenomena, including the subject matter of the present paper, the reader is referred to J. J. Thomson's Corpuscular Theory of Matter, p. 49 et seq.; O. W. Richardson's The Electron Theory of Matter, p. 407 et seq.; E. Bloch's La Théorie Electronique des Métaux (in a series of essays published under the title Les Idées Modernes sur la Constitution de la Matière, Villars, Paris); K. Baedeker's Die Elektrischen Erscheinungen in Metallischen Leitern (Braunschweig); also N. R. Campbell's Modern Electrical Theory, pp. 54–86.

2. Previous Theories and Their Limitations.

The equations deduced from the electron theory by Sir J. J. Thomson, and which are taken as a starting-point in the present discussion, are:

$$P_{12} = \frac{2\alpha T}{3\epsilon} \log \frac{N_1}{N_2}, \tag{1}$$

$$Q_{12} = \frac{2\alpha}{3\epsilon} \log \frac{N_1}{N_2}, \tag{2}$$

$$\sigma = \frac{2\alpha}{3\epsilon} \left\{ T \frac{d}{dT} (\log N) - \frac{1}{2} \right\}, \tag{3}$$

$$\kappa = \frac{\epsilon^2 N \lambda u}{4\alpha T}, \tag{4}$$

and

$$k = \tfrac{1}{3} \alpha N \lambda u. \tag{5}$$

From equations (4) and (5) we obtain the Wiedemann-Franz law that the ratio k/κ is a constant for all metals at any given temperature and the Lorenz law that this ratio is proportional to T, which laws together give

$$\frac{k}{\kappa T} = \frac{4}{3} \left(\frac{\alpha}{\epsilon} \right)^2. \tag{6}$$

The thermoelectric equations satisfy the following equations which were deduced from thermodynamical considerations by Lord Kelvin, namely,

$$P = QT, \tag{7}$$

and

$$\sigma_1 - \sigma_2 = T \frac{dQ_{12}}{dT}. \tag{8}$$

The constant multiplying factors on the right-hand side of equations (1) to (5), inclusive, have been given different values by different theorists, but in any case they only differ by simple numerical factors. Thus Drude[1] replaces $2\alpha/3\epsilon$ by $4\alpha/3\epsilon$ in equations (1), (2) and (3), and Lorentz,[2] assuming the Maxwellian distribution of velocities among the electrons, finds instead of equation (4) the equation

$$\kappa = \sqrt{\frac{2}{3\pi}} \left(\frac{\epsilon^2 \lambda N u}{\alpha T} \right), \tag{4a}$$

and instead of equation (5) the equation

$$k = \frac{8}{9} \sqrt{\frac{2}{3\pi}} (\alpha N \lambda u). \tag{5a}$$

[1] Ann. Phys., 1, 566, 1900 and 3, 369, 1900.

[2] Lorentz, The Theory of Electrons, pp. 63–67.

From (4*a*) and (5*a*) it follows that

$$\frac{k}{\kappa T} = \frac{8}{9}\left(\frac{\alpha}{\epsilon}\right)^2. \tag{6a}$$

The value of the ratio $k/\kappa T$ thus found is but two thirds of that found from the simple theory by Thomson and Drude. Since these differences in multiplying constants are of only secondary importance in connection with the present discussion they will be disregarded for the present. It may be remarked, however, that experimental data may, with the aid of the theory presented in this paper, enable one to discriminate between the different methods of approach to the problem and to select that one which agrees best with experiment.

It has usually been assumed either that N remained constant or else was either directly or inversely proportional to the square root of the absolute temperature. The first assumption was made in order to explain the optical properties of metals, the second was made by J. J. Thomson to account for the Thomson effect, and the last was made to account for the fact that at ordinary temperatures the temperature coefficient of resistance of a number of metals is approximately equal to 1/273 per Centigrade degree. From equation (4) it follows that if the electrical conductivity is inversely proportional to the absolute temperature, either N or λ must be inversely proportional to the square root of the absolute temperature, since $u = \sqrt{2\alpha T/m}$. We see no reason why λ should vary to any appreciable extent if the number of molecules does not change and the alteration in volume is quite small. Then N must change with temperature. But from the optical properties of metals it seems that N does not change.[1] So one has his choice: either N changes or it does not. But whether N is constant or is proportional to some power of the absolute temperature, the proportionality factor depending upon the material, certain results follow which are not in harmony with experiment. Some of these discrepancies are:

1. The thermo E.M.F. is a linear function of the temperature.
2. The thermoelectric power is constant for any given pair of metals.
3. The Thomson effect is the same for all metals at all temperatures.
4. The thermal conductivity of any metal is independent of the temperature.
5. The ratio $k/\kappa T$ is the same for all metals at all temperatures and within the range of ordinary temperatures is usually too small.

On the whole, the most that can be said for the theories so far published is that they show that these properties are to be expected, but they are wholly inadequate when it comes to quantitative measurements.

[1] Drude, Ann. Phys., 14, 951, 1904.

3. STATEMENT OF THE NEW THEORY.

The fundamental assumptions upon which this theory is based are

(1) That the number of free electrons in a metal *changes* with the temperature,

(2) That the number of positive centers with which the electrons collide, whether these centers are atoms, sub-atoms, molecules or groups of molecules, *changes* with the temperature, and

(3) That these positive centers take part in the transfer of heat but not of electricity.

The mathematical forms which have been selected to express the relations between the numbers of electrons and positive centers are

$$N = ae^{xT}, \tag{9}$$

and

$$n = be^{yT} \tag{10}$$

where a and b are positive constants, and nothing is postulated regarding the signs of x and y.

We are led to the first assumption by the fact that unless equations (1), (2) and (3) are entirely wrong, N must depend upon T. The exponential form of equation (9) is suggested by the logarithmic form of these three equations. The excellent agreement of the resulting equations with experiment indicates the probability that equation (9) is an accurate representation of the facts.

The assumption that the number of positive centers with which the electrons collide changes with the temperature is somewhat startling.[1] For our purposes it is unimportant whether these centers are atoms, sub-atoms, molecules or clusters of molecules. A great deal of uncertainty exists as to the states of aggregation in solids and liquids, and there is no *a priori* reason why the state of aggregation in a substance should not vary with the temperature of the substance. It is not necessary that all the centers shall be alike. A continual process of disintegration and recombination of the centers may be going on. If a theory based on this assumption should harmonize better with experiment than others, this circumstance would lend color to the assumption.

Remembering that, as in the kinetic theory of gases, $\lambda = f/nr^2$, where r is the radius of the positive centers and f is a constant, and substituting be^{yT} for n in equation (10), we obtain

$$\lambda = ce^{-yT}, \tag{11}$$

where $c = f/br^2$.

When $T = 0$, $N = a$, $n = b$ and $\lambda = c$. But when $T = \infty$, then

[1] Cf. Richardson's The Electron Theory of Matter, p. 467.

N and n are both infinite, and $\lambda = 0$. In practice, of course, T never approaches infinity, and since both x and y prove to be small, the values of N and n at, say, 2000° C. will probably seldom exceed 50 to 100 times the corresponding values at the absolute zero.

The third assumption seems reasonable from the fact that insulators conduct heat even though they do not conduct electricity, and have very few, if any, free electrons.

The only assumption involved in the theory of thermoelectricity here presented is the first, namely, that the number of free electrons is a function of the temperature. The second assumption is introduced to account for electrical conductivity, namely, that the number of positive centers is a function of the temperature. The third assumption, that the positive centers take part in the conduction of heat, is involved only in those portions of the theory which deal with thermal conductivity.

Equations (1) to (5), inclusive, are taken as the starting-points in the present discussion. This is not to be interpreted as indicating a preference on the part of the writer for one physicist's theory rather than that of another. In the light of our present knowledge, however, it seems that these equations are likely to be as valid as any of the others. Changing the constant factors has no effect upon the qualitative results of the theory presented here, and only to a minor extent upon the quantitative results.

4. PELTIER E.M.F.

Sir J. J. Thomson obtained equation (1) given above for the Peltier E.M.F. by assuming that electrons under the influence of an electric force flow across the boundary between two metals until the electric force is in equilibrium with the opposing pressure gradient at the boundary. The expression for the Peltier E.M.F. on the basis of the present extension of the simple theory is readily obtained by substituting in equation (1) the values of N_1 and N_2 given in equation (9), namely, $N_1 = a_1 e^{x_1 T}$ and $N_2 = a_2 e^{x_2 T}$. This gives

$$P_{12} = \frac{2\alpha T}{3\epsilon}\left\{\log\frac{a_1}{a_2} + (x_1 - x_2)T\right\}. \tag{12}$$

This equation may be rewritten in the form

$$P = AT + BT^2, \tag{12a}$$

or

$$P = P_0 + (273B + Q_0)t + Bt^2, \tag{12b}$$

where

$$A = \frac{2\alpha}{3\epsilon}\log(a_1/a_2),\ B = \frac{2\alpha}{3\epsilon}(x_1 - x_2),\ Q_0 = A + 273B,\ P_0 = 273Q_0,$$

and $t = T - 273$. P_0 is the Peltier E.M.F. at 0° C. and, as we shall see in the next section, Q_0 is the thermoelectric power of the pair of metals at 0° C.

The equations (12), (12*a*) and (12*b*) represent a parabola with its axis perpendicular to the axis of temperature. We should expect the Peltier E.M.F. to have a maximum value at the absolute temperature.

$$T' = -A/2B, \tag{13}$$

or in Centigrade degrees,

$$t' = -A/2B - 273 = -(273B + Q_0)/2B. \tag{13a}$$

The value of the Peltier E.M.F. at the temperature T' should be

$$P' = -A^2/4B. \tag{14}$$

If we knew the experimental form of the parabola it would be possible for us to calculate the values of A and B, and from these values we could obtain the value of the ratio a_1/a_2 and also of the difference $(x_1 - x_2)$. In practice, however, it will be very much simpler to obtain these values from the thermo E.M.F.

5. Thermoelectric Power.

The equations for the thermoelectric power are readily obtained from the corresponding ones for the Peltier E.M.F. by dividing by T (see equation (7)). From equations (12), (12*a*) and (12*b*) we thus obtain

$$Q_{12} = \frac{2\alpha}{3\epsilon}\left\{\log\frac{a_1}{a_2} + (x_1 - x_2)T\right\}, \tag{15}$$

$$Q = A + BT, \tag{15a}$$

and

$$Q = Q_0 + Bt, \tag{15b}$$

where A, B and Q_0 have the same values as in the preceding section. These equations represent quite accurately, by a suitable choice of constants, the thermoelectric power of a thermocouple consisting of almost any pair of metals.

6. Thermo E.M.F.

The expression for the thermo E.M.F. is obtained from that for the thermoelectric power by integrating the latter with respect to T. If E is the thermo E.M.F. between two metals 1 and 2, when their junctions are at the temperature T_1 and T_2, then

$$E = \int_{T_1}^{T_2} Q dT,$$

whence

$$E = \frac{2\alpha}{3\epsilon}\left\{\left(\log\frac{a_1}{a_2}\right)(T_2 - T_1) + \frac{1}{2}(x_1 - x_2)(T_2^2 - T_1^2)\right\}. \tag{16}$$

If we put $T_1 = 0$ and $T_2 = T$, then equation (16) becomes

$$E = \frac{2\alpha}{3\epsilon}\left\{ T \log \frac{a_1}{a_2} + \frac{1}{2}(x_1 - x_2)T^2 \right\}, \tag{17}$$

where E is the thermo E.M.F. between two junctions at 0° and $T°$ absolute, respectively. Equation (17) may be rewritten in the form

$$E = AT + \tfrac{1}{2}BT^2. \tag{17a}$$

Substituting $t + 273°$ for T_2 and 273 for T_1 in equation (16) we obtain

$$E = Q_0 t + \tfrac{1}{2}Bt^2, \tag{16a}$$

where E is the thermo E.M.F. between two junctions at 0° C. and $t°$ C., respectively.

Equations (17), (17*a*) and (16*a*) represent a parabola with its axis perpendicular to the axis of temperature. The maximum value of E occurs at the neutral temperature, which is therefore given by the equation

$$T' = -A/B, \tag{18}$$

or

$$t' = -Q_0/B. \tag{18a}$$

The thermo E.M.F. of the couple when one junction is at 0° C. and the other is at the neutral temperature is given by the equation

$$E' = -Q_0^2/2B. \tag{19}$$

Experimentally it is found that the thermo E.M.F. between any two metals is quite accurately represented by a parabola with its axis perpendicular to the axis of temperature, that is, by equations of the type deduced above, where A and B may either positive or negative. Thus we see that the equations here deduced for thermoelectric power and thermo E.M.F. are in agreement with the experimental facts. And since equation (7) has been shown to be true both experimentally and theoretically, the equations for the Peltier E.M.F. must also be in agreement with the experimental facts. From our theory we see that A is positive or negative according as a_1 is greater or less than a_2. Similarly, B is positive or negative according as x_1 is greater or less than x_2.

From the known values of A and B obtained from experiment we may calculate the values of a_1/a_2 and $(x_1 - x_2)$ by means of the following equations:

$$a_1/a_2 = e^{3\epsilon A/2\alpha}, \tag{20}$$

and

$$x_1 - x_2 = 3\epsilon B/2\alpha. \tag{21}$$

It may be remarked in passing that if N were a constant different for different metals, or if N were proportional to any power of the absolute

temperature, the proportionality factor being different for different metals, then the thermoelectric power would be constant and the thermo E.M.F. would be proportional to the difference between the absolute temperatures of the two junctions. These conclusions, however, are contrary to experiment.

7. THOMSON EFFECT.

When we substitute ae^{xT} for N in equation (3) we obtain

$$\sigma = \frac{2\alpha}{3\epsilon}(Tx - \tfrac{1}{2}). \tag{22}$$

Since for practically all metals the absolute value of σ is considerably less than $\alpha/3\epsilon$, it follows that x must be positive. Hence, we may conclude that *in order to account for the Thomson effect it is necessary to assume that the number of free electrons in a metal increases with the absolute temperature.* So long as x is positive, σ will have the same sign as $(Tx - \tfrac{1}{2})$, and the absolute value of σ, when it is negative, cannot be greater than $\alpha/3\epsilon$. On the other hand, σ may have any positive value when x is positive. In the case of certain alloys[1] it appears that σ is negative and greater than $\alpha/3\epsilon$. In such cases x must be negative.

Differentiating equation (22) with respect to T, we obtain

$$\frac{d\sigma}{dT} = \frac{2\alpha x}{3\epsilon}. \tag{23}$$

From equation (23) it appears that *the Thomson effect has a temperature coefficient, and that this temperature coefficient is normally positive.* Qualitatively at least, this result is in harmony with some of the best experimental results such, for example, as those obtained by Berg[2] on copper. In the case of the alloys mentioned above, which have abnormally high negative values of the Thomson effect, Laws found that the temperature coefficients were negative. This is in harmony with our theory.

From the value of the Thomson effect at any temperature it is possible to calculate the value of x. Solving equation (22) for x we obtain

$$x = \frac{3\epsilon\sigma + \alpha}{2\alpha T}. \tag{24}$$

Generally speaking, Tx cannot be very far different from $\tfrac{1}{2}$ at ordinary temperatures, since σ is usually quite small in comparison with $\alpha/3\epsilon$. This being so, let us assume that $Tx = \tfrac{1}{2}$ and that $T = 300°$ absolute (27° C.). Then $x = 0.001667$. Substituting this value of x in equation

[1] Laws, Phil. Mag., 7, pp. 560–578, 1904, and Caswell, PHYS. REV., N.S., XII., pp. 231–237, 1918.

[2] Ann. Phys., 32, pp. 477–519, 1910.

(9), we find the ratio of the value of N at any temperature $(T + 1)$ to its value at the temperature T to be 1.0017. Or, to use a somewhat larger temperature interval, the ratio of N at $(t + 100)°$ C. to its value at $t°$ C. is 1.181. For a temperature interval of 1000° C. the ratio is 5.294. Assuming 0.002 as a probably maximum value of x for a pure metal, we find the corresponding values of the ratio for a temperature interval of one degree Centigrade to be 1.0020, for a 100° C. interval 1.2214, and for a 1000° C. interval 7.389.

If our theory is correct, the Thomson effect is a linear function of the temperature which approaches the common value for all metals at the absolute zero of $\sigma = -\alpha/3\epsilon$. In case we should have used $4\alpha/3\epsilon$ instead of $2\alpha/3\epsilon$ in equations (1), (2) and (3), then σ should have a different limiting value. The same is true if any other factor is used instead of $2\alpha/3\epsilon$. If this limiting value of σ can be determined, then we have a means of selecting the best from among the different equations proposed.

It follows at once from equation (22) that

$$\sigma_1 - \sigma_2 = \frac{2\alpha T}{3\epsilon}(x_1 - x_2), \tag{25}$$

or

$$\sigma_1 - \sigma_2 = BT, \tag{25a}$$

these equations being in the form of equation (8). It is obvious that the metal having the more positive value of x will have the more positive value of σ, and *vice versa*. Consequently, if we were to arrange a series of metals in the order of the slope of the corresponding lines in a thermo-electric power diagram, the metals should also be arranged in the order of their Thomson effects at any given temperature.

8. Electrical Conductivity.

In the preceding sections the only assumption which has been employed is that the number of free electrons is a function of the temperature, and the satisfactory agreement between the theory and experiment seems to prove the wisdom of selecting the expression ae^{xT} to represent this number at any temperature T. No assumption was made as to the sign of x, but we have found that to account for the Thomson effect in most substances x must be positive. To this assumption we now add a second, namely, that the number of positive centers is a function of the temperature, and, in consequence, the mean free path of the electrons is a function of the temperature. Any discrepancies between theory and experiment which appear in this section must, therefore, arise not from the first assumption, but from the second.

Substituting the value of N from equation (9), the value of λ from equation (11), and $u = (2\alpha T/m)^{1/2}$ in equation (4), we obtain as the value of the electrical conductivity

$$\kappa = \frac{\epsilon^2 ac}{2\sqrt{2\alpha m}} e^{(x-y)T} \cdot T^{-1/2}, \tag{26}$$

which we shall rewrite in the form

$$\kappa = Ce^{-zT} \cdot T^{-1/2}, \tag{26a}$$

where $C = \epsilon^2 ac/2(2\alpha m)^{1/2}$, and $z = y - x$. Both C and z are constants for any given metal.

Since the electrical conductivity of pure metals within the range of ordinary temperatures is roughly inversely proportional to the absolute temperature, it follows from equation (26a) that the exponential factor on the right-hand side of the equation must decrease with increase of temperature. In order that this shall be so, z must be positive or $(x - y)$ must be negative. But since x is positive in the case of pure metals, y must also be positive and greater than x. Hence, we conclude that *in the case of pure metals both the number of free electrons in the metal and the number of positive centers with which they collide increases with the temperature, the number of positive centers, in general, increasing faster than the number of electrons.*

In the case of alloys the electrical conductivity cannot be said to bear any general relation to the temperature. In fact in the case of some alloys, such as manganin, the temperature coefficient is exceedingly small. In such cases the exponential factor may increase with the temperature. That is, if x is positive, then y is either positive and less than x or else y is negative, but if x should happen to be negative, as we have seen is probable in the case of some alloys, then y is also negative but numerically greater than x. The case when both x and y are positive seems the most likely to occur, since this is the rule for pure metals. In any case we may conclude that *in some substances, particularly alloys, the number of free electrons increases with the temperature faster than the number of positive centers with which they collide.*[1]

The electrical conductivity of carbon, which though not a metal conducts metallically, increases rather rapidly with the temperature. This means that z for carbon has a comparatively large negative value. This probably indicates a large positive value of x with a smaller positive, or possibly negative, value of y. An abnormally large value of x corre-

[1] A good account of the electrical properties of alloys is given in Baedeker's Elektrischen Erscheinungen in Metallischen Leitern. Lord Rayleigh (Scientific Papers, Vol. IV., p. 232) has suggested that the resistance of alloys is unduly high owing to a "false resistance" arising from the Peltier effect between non-homogeneous parts of the metal.

sponds to an abnormally large positive value of the Thomson effect.

Since ρ is the reciprocal of κ it follows that

$$\rho = \frac{1}{C} e^{zT} \cdot T^{1/2}, \tag{27}$$

whence

$$z = \frac{1}{T}(\log C + \log \rho - \tfrac{1}{2} \log T). \tag{28}$$

If ρ is proportional to T, as is assumed but is not strictly true to fact, then

$$z = \frac{1}{T}(\log (CD) + \tfrac{1}{2} \log T), \tag{28a}$$

where ρ is put equal to DT.

From equation (28*a*) it appears that either ρ is not proportional to T or else z is not constant as assumed, but is a function of T. Whenever the value of z is greater than the right-hand side of equation (28*a*) the resistivity increases faster than the absolute temperature, but when the reverse is true the resistivity increases more slowly than the absolute temperature.

From equation (27) it is obvious that the resistivity of a metal approaches zero at the absolute zero, and increases continuously with the temperature providing z is positive. In case z is negative the resistivity should have a maximum value when $T = -(1/2z)$.

Since the factors a and c, which are contained in the value of C, are as yet undetermined, we cannot use equation (28*a*) to calculate the value of z. But since we know how ρ varies with T we may write

$$\frac{\rho_1}{\rho_0} = e^{z(T_1 - T_0)} \left(\frac{T_1}{T_0}\right)^{1/2}, \tag{29}$$

where ρ_1 and ρ_0 are the resistivities at $T_1°$ and $T_0°$ absolute, respectively. Putting $T_1 = T_0 + 1$, and solving for z, we obtain

$$z = \log \frac{\rho_1}{\rho_0} - \tfrac{1}{2} \log \left(1 + \frac{1}{T_0}\right). \tag{29a}$$

If we denote the temperature coefficient of resistance at T_0 by β, we may rewrite equation (29*a*) thus:

$$z = \log (1 + \beta) - \tfrac{1}{2} \log \left(1 + \frac{1}{T_0}\right), \tag{29b}$$

or as a first approximation which gives a result about one half per cent. too high

$$z = \beta - \frac{1}{2T_0}. \tag{29c}$$

We find the temperature coefficient of resistivity of copper given as 0.00428 at 18° C., *i. e.*, $T_0 = 291$, and so z is found to be 0.002545 if we use equation (29*b*), but is found to be 0.00256 if we use equation (29*c*).

From the ratio of the resistivities of two metals at any temperature T we may determine the ratio c_1/c_2, thus:

$$\frac{c_1}{c_2} = \frac{\rho_2 a_2}{\rho_1 a_1} e^{(z_1 - z_2)T}. \tag{30}$$

Since all the quantities on the right can be determined the ratio c_1/c_2 can be calculated. It should be noted, however, that the numerical values which we obtain for a_1/a_2, and consequently for c_1/c_2, depend upon whether we use $2\alpha/3\epsilon$ or some other multiplying factor in equations (1), (2) and (3).

9. THERMAL CONDUCTIVITY.

We now proceed to introduce the third assumption, namely, that the molecules or, more generally, the positive centers, whether these are atoms, sub-atoms, molecules or groups of molecules, take part in the transmission of heat, although they have no part in the transmission of electricity in solid bodies. In the simple equation (5), namely, $k = \frac{1}{3}\alpha N \lambda u$, N, λ and u refer specifically to the electrons. A fundamental assumption of the electron theory is the equi-partition of energy among the electrons and molecules, but there are certain reasons why we are at present unable to assign values to the molecular quantities corresponding to N, λ and u. Indeed for our present purpose it is unimportant whether such values can be assigned. Obviously, there is the probability that heat is transmitted by the molecules, or positive centers, by radiation as well as by conduction. What fraction of the total heat transmitted is transmitted by radiation we are unable to determine. For the present it remains an open question whether the equi-partition of energy law applies to the molecules or to the positive centers.

It is rather obvious that the mean free paths and the velocities of the positive centers, or of the molecules, will vary in the same directions as λ and u, respectively. We shall assume, for simplicity, that λ_1 is directly proportional to λ, and that u_1 is directly proportional to u, where λ_1 is the mean free path of the positive centers, or molecules, as the case may be, and u_1 is the corresponding mean square speed. We may then rewrite equation (5), substituting $N + n$ for N and introducing a constant ω which includes the proportionality factors connecting λ and λ_1, and u and u_1, and also the ratio of the total amount of heat transmitted by the molecules to that conducted by them. We thus obtain

$$k = \tfrac{1}{3}\alpha u \lambda (N + \omega n). \tag{31}$$

Equation (31) simply means that in view of our ignorance of the behavior of these positive centers, we feel justified in assuming that the fraction of the total heat transmitted by them is proportional to their number.

Replacing N by ae^{xT}, n by be^{yT}, λ by ce^{-yT} (see equations (9), (10) and (11)), and u by $(2\alpha T/m)^{1/2}$, equation (31) reduces to

$$k = \frac{\sqrt{2\alpha}}{3\sqrt{m}} ac \left(e^{(x-y)T} + \frac{\omega b}{a} \right) T^{1/2}. \tag{32}$$

It is at once apparent that in the case of pure metals the exponential factor in the first term on the right-hand side of equation (32) tends to make k decrease as T increases, since $(x - y)$ is negative, while the factor $T^{1/2}$ tends to make both terms increase as T increases. So k may either increase or decrease with increase in temperature.

10. The Wiedemann-Franz and Lorenz Laws.

We have already seen that the Wiedemann-Franz law coupled with that of Lorenz leads to the relation that $k/\kappa T = a\ constant$. Substituting the values of k and κ from equations (32) and (26), respectively, we obtain

$$\frac{k}{\kappa T} = \frac{4\alpha^2}{3\epsilon^2} \left(1 + \frac{\omega b}{a} e^{xT} \right). \tag{33}$$

When $\omega = 0$, this equation reduces to equation (6) as a special case. Equation (33) leads us to expect that the experimentally determined value of the ratio will always be greater than that calculated from the simple theory. Assuming the validity of equation (6), the experiments of Jaeger and Diesselhorst[1] on thirteen metals and three alloys gave values in every case, except that of aluminum, greater than we should expect from the simple theory; but if we assume the validity of equation (6a) the discrepancy is much greater, even aluminum being about thirty per cent. too high. It has been objected that the amount of heat transmitted by the positive centers, whatever they may be, must be much too small to account for the discrepancies between Jaeger and Diesselhorst's experiments and the simple theory. But this objection is based on the assumption that the heat so transmitted must be approximately the same as that transmitted by an insulator. This does not necessarily follow. If there are practically no free electrons in an insulator and there are large numbers of them in conductors, is it not reasonable to suppose that there may be more freedom of movement among the molecules in a conductor than among those in an insulator?

The minimum value which the right-hand side of equation (33) can have is $4\alpha^2(1 + \omega b/a)/3\epsilon^2$. This seems out of harmony with the results

[1] Sitzungsber. Berlin, 1899, p. 719.

obtained by Meissner[1] at very low temperatures, since he found that for copper at 20° absolute the value of the ratio $k/\kappa T$ was but one seventh of its value at 0° C., the value at 0° C. being only slightly greater than $4\alpha^2/3\epsilon^2$.

If the subscripts 1 and 2 refer, respectively, to the temperature T_1 and T_2, then

$$\frac{k_2/\kappa_2}{k_1/\kappa_1} = \frac{\left(1 + \frac{\omega b}{a} e^{\epsilon T_2}\right) T_2}{\left(1 + \frac{\omega b}{a} e^{\epsilon T_1}\right) T_1}. \tag{34}$$

According to the simple theory this should be

$$\frac{k_2/\kappa_2}{k_1/\kappa_1} = T_2/T_1. \tag{34a}$$

Jaeger and Diesselhorst, working between the temperatures of 18° C. and 100° C., *i. e.*, between 291° and 373° absolute, found instead of the theoretical value of the ratio on the left-hand side of equation (34*a*), viz., $T_2/T_1 = 1.28$, that eight of the thirteen metals tested gave values greater than 1.28, two of them, platinum and palladium, giving values of 1.35, two gave values of 1.28, one of 1.27, one of 1.26 and one, bismuth, of 1.12. The three alloys tested gave results less than 1.28. Whenever y is greater than x, as we have seen is the case in pure metals, equation (34) leads us to expect the ratio to be greater than 1.28. In the majority of cases this seems to be true. But in the case of an alloy, such as manganin, which has a very small temperature coefficient of resistance, x is greater than y, and equation (34) leads us to expect the ratio to be less than 1.28. This is actually the case. In the case of manganin the ratio is 1.21.

11. Discussion of the Theory.

In this section the author wishes to make some general observations concerning the theory here presented. In the first place, we see that, since the equations are of the proper form and the values of the constants involved can be determined from experimental data, the agreement of the theory with the phenomena of the Peltier and Seebeck effects is not only qualitative but quantitative as well. Not only do the values of the constants so determined indicate that, in general, the number of free electrons increases with the temperature, but this is what we might expect, since the kinetic energy and, consequently, the agitation of the molecules increases with the temperature.

In a previous paper the author has shown that either (1) the electrons

[1] Deutsch. Phys. Gesell., Verh. 16, 5, pp. 262–272, 1914.

which take part in thermoelectric phenomena are different from those which take part in electric conduction, or (2) the mean free path of the electrons in an alloy is noticeably different from that in a pure metal, one of the constituents of the alloy. The former statement seems unreasonable, while the latter is plausible if the formation of an alloy involves the regrouping of the atoms or molecules. Thus the writer was led to the conclusion that in some way a change is brought about in the mean free path of the electrons. The introduction of the exponential value of N from equation (9) into equation (4) makes the resulting change in the electrical conductivity in the opposite direction to that in which it actually occurs. So we have adopted the hypothesis that the mean free path of the electrons as well as their number is a function of the temperature. The change in the mean free path may be thought of as being brought about in either of two ways, always assuming that the number of collisions between electrons is negligible in comparison with the number between electrons and the positive centers. Either the size of the positive centers may change or their number. Assuming that the size changes but not the number we are led to conclusions which do not agree as well with experiment as do the conclusions which we arrive at by assuming that the number of positive centers is a function of the temperature. The author is inclined to believe that the exponential form of the function which has been employed in this paper is a fair representation of the facts, if temperatures near which marked changes in the structure of the metal occur, such as eutectic-points and melting-points, are excluded. In this connection it should be noted that the Peltier E.M.F. and the thermo E.M.F., both of which we assume depend only upon the concentration of the electrons, are not discontinuous functions of the temperature at the melting-point, but it appears that the electrical conductivity of a metal changes markedly as it passes from the solid to the liquid state. In the case of a number of metals, *e. g.*, cadmium, lead, potassium, sodium, tin and zinc, the electrical conductivity in the solid state at the melting-point is about one half the value in the liquid state at the same temperature. Exceptions are bismuth and antimony. In both of these the conductivity is approximately doubled as the substances passes from the solid to the liquid state. The usual case, that of decrease in conductivity in passing from the solid to the liquid state, is apparently due to a sudden increase in the number of positive centers. This is what one might expect since there is, apparently, a reduction in the forces of cohesion.

It seems probable that at low temperatures the molecules of a metal are gathered in clusters which act as single positive centers and that

as the temperature is raised the increased activity of the molecules causes these clusters to break up slowly. The complete theory should, therefore, take account of the change in the cross-sections of the clusters as they break up as well as the change in their number. What the change in the cross-section is must depend upon the number and arrangement of the molecules in each cluster, and any general expression must represent a mean rate of change in the cross-sections. Since the number of positive centers must increase faster than their average cross-section decreases, the change in the former is more important than that in the latter.

In the theory as developed in this paper no allowance has been made for the expansion of the metal as the temperature is raised. The complete theory ought to take account of this expansion. The correction, however, is likely to be quite small.

It is obvious that an exhaustive study of the quantitative relations of this theory and experiment ought to be made. We have shown that qualitatively it is capable of explaining all of the phenomena considered if we exclude very low temperatures. It is also capable of explaining each of these phenomena separately quantitatively, but it remains to be seen to what extent the values of the constants involved are identical when different phenomena are compared. The writer is now carrying out the necessary computations to put the theory on a quantitative basis and hopes to publish the results of this work in the near future.

Physical Laboratory,
University of Oregon,
February, 1919.

THE AUDION AS A CIRCUIT ELEMENT.

BY H. W. NICHOLS.

SYNOPSIS.—The functional equations for the three-element audion are used to deduce the actions taking place in any circuit containing the audion. The equations for small variations in the general network containing audions are developed and simple equivalent circuits to replace the tube are shown. Next the effects of the capacities between elements are worked out and also some examples of amplifiers and oscillation generators.

THE three-element thermionic tube has come into such general use in radio telegraphy and telephony as well as in wire telephony and other fields that it seems worth while at the present time to publish some of those relations, holding between its characteristics and those of the connected electrical circuits, which are used in the design of amplifying, oscillating and detecting systems.

In this paper will be considered only those actions which may be sufficiently well described by supposing the variations in plate and grid currents and voltages to be small. In this discussion the methods adopted in a previous paper[1] will be shown in their application to vacuum tube circuits, in which application, as a matter of fact, their greatest practical use has been found.

The first figure shows a conventional circuit drawing of an audion in which the grid and plate potentials, with filament potential as zero, are denoted by v and V respectively, while the corresponding currents are denoted by i and I. A discussion of the operation of this device is unnecessary, since several papers have appeared describing the construction and operation in considerable detail. It has been found that, as long as there is an excess of electrons supplied by the filament so that temperature saturation is maintained, the plate current is represented with considerable accuracy by a function of a *single* variable, thus:

$$I = F(V + \mu v + c),$$

in which c is a constant which depends partly upon the contact differences of potential of the elements in the tube and μ is another constant which is characteristic of the structure. In many forms which the device may take the plate current is very approximately proportional to the square

[1] PHYS. REV., Aug., 1917.

of the variable above, but for the purpose of this discussion it is not necessary to so limit it.

The grid current depends also upon the two potentials, but its functional form is not known. For this discussion it is sufficient to recognize that it is such a function and write it:

$$i = f(V, v).$$

The problem to be considered in this paper is now the following. An audion is connected into an electrical network in any manner, that is, its three terminals are joined by any system of impedances; certain grid and plate voltages are impressed upon it with the result that certain currents, determined by the functional equations above, flow to plate and grid; and then it is required to describe the small variations about

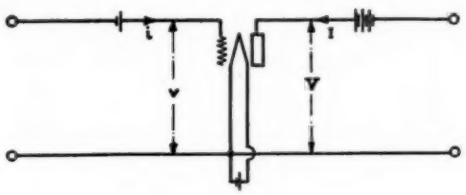

Fig. 1.

this steady state which will take place when the system is acted upon by arbitrary electromotive forces or otherwise disturbed. This is the problem of amplifiers and oscillation generators with the limitation that the amplitude of oscillation shall be small. While this limitation is serious in some cases, for example if it is desired to find the maximum power output of the device, still a great deal of information concerning the operation of the actual device may be obtained by thus studying the ideal case, which, in fact, is the only one which lends itself to simple and general treatment from the point of view of electrical networks.

In Fig. 2 is shown the audion connected into the network. In this figure the impedances Z_1, Z_2, Z_3, may be of any form whatever and are not restricted to single conducting paths as indicated. They are supposed only to be such circuits that it is possible to write an equation of the form $ZI = e$, connecting the current entering the terminals and the E.M.F. producing this current when the circuit is isolated. Certain electromotive forces, E, are supposed acting in each branch and the three circuits are coupled to one another by mutual impedances, M_{jk}, between impedance j and impedance k. These mutual impedances are defined, as usual, by the statement that a unit current in branch j induces an E.M.F. M_{jk} in branch k. Both self and mutual impedances are in the

general case operators, functions of $p = d/dt$, as used in the paper above cited.

If in this network the three currents are chosen as shown, we may wirte down the network equations in terms of them as below:

$$Z_1(I_1 + I_3) + v = E_1 + M_{12}(I_2 - I_3) - M_{13}I_3$$
$$Z_2(I_2 - I_3) + V = E_2 + M_{12}(I_1 + I_3) + M_{23}I_3$$
$$Z_3I_3 + V - v = -M_{13}(I_1 + I_3) + M_{23}(I_2 - I_3).$$

These equations are of course exact and hold for all conditions; however, because they are not linear, their solution is somewhat complicated and it is preferable to obtain the first and approximate idea of the be-

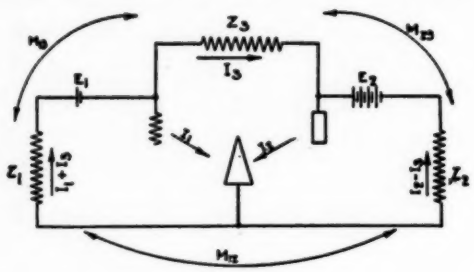

Fig. 2.

havior of the network by considering only small changes in the currents from their steady or mean values. This amounts to considering current variations over a part of the characteristic curve so small that it may be taken to coincide with the tangent at the given operating point and consequently the solutions obtained will not describe any effects which depend upon the curvature of the characteristic, such effects, for example, as the detection of signals.

Suppose then that in the departure from the steady values I_1 changes to $I_1 + x_1$, etc., these changes being small and produced by superposed electromotive forces e_1, etc. We shall then have

$$\delta v = \frac{\partial v}{\partial I_1}x_1 + \frac{\partial v}{\partial I_2}x_2, \qquad \text{etc.}$$

Substituting these values in the network equations, there will result a set of linear differential equations, with independent variable t, of the type:

$$Z_1(x_1 + x_3) + \frac{\partial v}{\partial I_1}x_1 + \frac{\partial v}{\partial I_2}x_2 = e_1 + M_{12}(x_2 - x_3) - M_{13}x_3$$

. . . . . .

which set may be conveniently represented in the following tabular form:

x_1	x_2	x_3	
$Z_1 + \frac{\partial v}{\partial I_1}$	$-M_{12} + \frac{\partial v}{I_2 \partial}$	$Z_1 + M_{12} + M_{13}$	e_1
$-M_{12} + \frac{\partial V}{\partial I_1}$	$Z_2 + \frac{\partial V}{\partial I_2}$	$-Z_2 - M_{12} - M_{23}$	e_2
$-M_{13} + \frac{\partial V}{\partial I_1} - \frac{\partial v}{\partial I_1}$	$-M_{23} + \frac{\partial V}{\partial I_2} - \frac{\partial v}{\partial I_2}$	$Z_3 + M_{13} + M_{23}$	e_3

These are the network equations for small disturbances but it is convenient to throw them into another form which takes account of the physical meaning of some of the terms. To do this, note that $\partial v/\partial I_1$ is evidently the resistance, r, of the grid circuit under the given operating conditions, and $\partial V/\partial I_2$ is the resistance, R, of the plate circuit under the same conditions. From the characteristic equations we find by the usual methods, the further relations:

$$\frac{\partial v}{\partial I_1} = \frac{F'}{J} = r, \qquad \frac{\partial v}{\partial I_2} = \frac{-1}{J}\frac{\partial f}{\partial V},$$

$$\frac{\partial V}{\partial I_1} = -\frac{\mu F'}{J} = -\mu r, \qquad \frac{\partial V}{\partial I_2} = \frac{1}{J}\frac{\partial f}{\partial v} = R,$$

where

$$J = F'\left(\frac{\partial f}{\partial v} - \mu\frac{\partial f}{\partial V}\right).$$

Now since $\partial V/\partial I_1$ is the E.M.F. induced in the plate circuit through the tube by unit current in the grid circuit and rx_1 is the corresponding increment, δv, in grid potential, it follows from the above relations that one action of the tube is to introduce into the plate circuit an effective E.M.F. equal to μ times the grid voltage variation.

Also, since $\partial v/\partial I_2$ is the E.M.F. introduced into the grid circuit through the tube by unit current in the plate circuit, we find that another action of the tube is to introduce the voltage

$$\frac{\partial v}{\partial I_2}x_2 = -\frac{1}{J}\frac{\partial f}{\partial V}x_2 = -Rx_2\frac{\partial f/\partial v}{\partial f/\partial V} = -\delta V\cdot\frac{\partial f/\partial V}{\partial f/\partial v}$$

into the grid circuit. Thus the two mutual impedances of the tube are in general different in the two directions, which accounts for the amplifying properties of the device as explained in the paper already mentioned. This reverse action, from plate circuit to grid circuit, is often ignored in discussions of the audion and it is assumed that, since the plate current is a function of $V + \mu v$ only, the action of the device is summed up in the statement that the grid is μ times as effective as the plate in pro-

ducing current changes. This action is, however, the only one if, for example, the grid current is independent of plate potential: there is then no reaction upon the grid circuit (neglecting capacity from grid to plate, which will be considered later) and the tube is a purely unilateral device. Since in practice this condition often holds very approximately, it is often legitimate to neglect $\partial v/\partial I_2$ and consequently to consider the tube as a device which, for small current changes, simply introduces into the

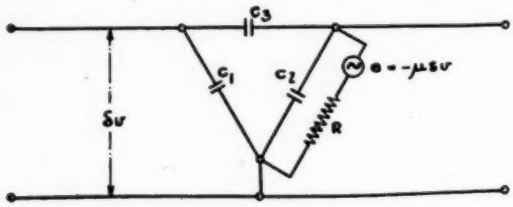

Fig. 3.

plate circuit (just where will develop later) an E.M.F. equal to μ times the change in grid potential. When this condition holds the last equations are still further simplified into:

x_1	x_2	x_3	
$Z_1 + r$	$- M_{12}$	$Z_1 + M_{12} + M_{13}$	e_1
$- M_{12} - \mu r$	$Z_2 + R$	$- Z_2 - M_{12} - M_{23}$	e_2
$+ M_{13} - (\mu + 1)r$	$- M_{23} + R$	$Z_3 + M_{13} + M_{23}$	e_3

Equivalent Circuit of the Tube.—When the grid current does not vary appreciably with plate voltage it is possible to use a very simple equivalent circuit for the audion itself. This circuit is shown in Fig. 3 in which the resistance R of the plate circuit is shown between plate and filament and the three condensers, c_1, c_2, c_3 represent respectively the internal capacities between grid-filament, plate-filament and grid-plate. These capacities must obviously be taken into account at sufficiently high frequencies. Under the given conditions r is effectively infinite. Located in the impedance of the plate circuit is an alternator whose E.M.F. is equal to μ times the voltage, δv, produced across the grid-filament terminals. If this circuit is worked out it will be found that it is the exact equivalent of the actual tube under the given conditions. The feature of the circuit is the location of the fictitious E.M.F. between filament and plate, and the network will serve for the solution of tube problems as long as the electromotive forces impressed upon the network are small enough not to violate the conditions. The use of this equivalent avoids the necessity of setting up the complete equations.

It is obvious that, as a closer approximation, an equivalent circuit may be drawn in which another alternator is used to represent the reaction upon the grid circuit, but for practical use it has been found that this complication is in most cases unnecessary. Except at the very highest frequencies this network may be still further simplified by omitting the condenser c_2 since its capacity is but a few micro microfarads and it is shunted by the resistance R. The other condensers are, however, very important, even at moderate frequencies, and this will be shown by two examples.

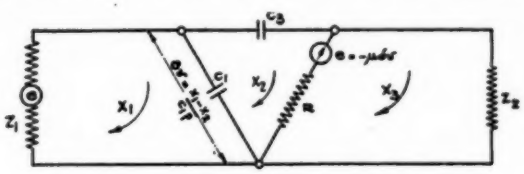

Fig. 4.

1. *The Input Impedance of an Audion Amplifier.*—Fig. 4 represents the equivalent circuit of an audion for frequencies below a few million and with the grid maintained negative with respect to the filament so that the input *resistance* is infinite. The output circuit is closed through an impedance Z_2. If there were no connection between the plate and grid circuits the impedance of the amplifier, as measured from the input terminals, would be simply that of the condenser c_1. The grid-plate capacity, however, modifies this result greatly. This impedance will be worked out and to do this the network equations, in terms of the mesh currents x_1, x_2, x_3 are given below with an E.M.F. e in the input circuit. p represents d/dt as usual and the fictitious E.M.F. in the tube resistance is μ times the voltage drop, $(x_1 - x_2)/c_1p$, over the condenser c_1. The sign is such that a positive grid tends to increase the plate current.

x_1	x_2	x_3	
$Z_1 + \frac{1}{c_1p}$	$-\frac{1}{c_1p}$	0	o
$-\frac{1+\mu}{c_1p}$	$\frac{1+\mu}{c_1p} + \frac{1}{c_3p} + R$	$-R$	o
$\frac{\mu}{c_1p}$	$-R - \frac{\mu}{c_1p}$	$R + Z_2$	e

If D is the operational determinant of this system and D_{11} the minor of the element (1, 1) the input impedance is

$$Z = D/D_{11} \quad \text{with} \quad Z_1 = 0,$$

and this works out to be

$$Z = \frac{1}{c_1 p} \frac{1 + Wc_3 p}{1 + Wc_3 p + \frac{c_3}{c_1}\left(1 + \mu - \mu \frac{W}{Z_2}\right)},$$

in which W is equal to $RZ_2/(R + Z_2)$, the impedance of R and Z_2 in parallel. Note that if the grid-plate capacity is zero, this reduces to $1/c_1 p$ which is the impedance of the grid-filament condenser. This impedance is in the operational form; to find the impedance to steady alternating currents of frequency $n/2\pi$, p is to be replaced by in where i is the imaginary unit.

To save space only a few consequences will be noted, since it is easy to draw conclusions from the formula. In the first place, even at low frequencies (when the terms containing p as a factor are negligible) the impedance is charged into

$$\frac{1}{c_1 p} \frac{1}{1 + \frac{c^3}{c_1}\left(1 + \mu - \mu \frac{W}{Z_2}\right)}; \quad p \text{ small.}$$

In some cases this impedance only remotely resembles a capacity reactance; for instance if the output impedance, Z_2, is inductive, the impedance may have a negative resistance component. This means that the amplifier is likely to sing under these conditions, and in fact the tendency of a tube to oscillate "through its internal capacities" has often been observed.

At extremely high frequencies the formula shows that the impedance again approaches a capacity reactance, as it obviously should do since then the condenser c_1 practically short-circuits the current entering the input terminals. It is instructive to work out the impedance under various simplifying assumptions, and in the case of amplifiers which sing the solution of the difficulty will often be found in this manner.

2. *Amplification at High Frequencies.*—As a second example of the use of the equivalent circuit of the tube, suppose the circuit of Fig. 4 is to be used to produce in the impedance Z_2 an amplified current under the influence of the generator e in the input circuit. It is clear from inspection that for very high frequencies the condenser c_3 will have such a low impedance that the amplifying action of the tube will be seriously impaired. To get a quantitative measure of the effect of varying the frequency, consider what is meant by amplification. If the tube were a perfect unilateral amplifier a current x_1 in mesh 1 would produce a certain E.M.F., e_3, in mesh 3, while a current x_3 in mesh 3 would produce no E.M.F. in mesh 1. On the other hand, if the network were a simple

transforming one (no amplification), the same E.M.F.'s would be produced by the same currents in either direction through the network. Hence, defining the two mutual impedances in the usual way as

$$M_{13} = \frac{e_3}{x_1}, \qquad M_{31} = \frac{e_1}{x_3},$$

it is clear that for a perfect unilateral amplifier $M_{31}/M_{13} = 0$, while for a perfect transforming network this ratio is unity. The above ratio of the two mutual impedances is therefore a measure of the failure of the tube as an amplifier.

From the network determinant, already used, we find this ratio to be

$$\frac{M_{31}}{M_{13}} = \frac{D_{31}}{D_{13}} = \frac{1}{1 - \dfrac{\mu}{c_3 R p}},$$

or for simple harmonic currents of frequency $n/2\pi$:

$$\frac{M_{31}}{M_{13}} = \frac{1}{1 + \dfrac{i\mu}{Rc_3 n}}.$$

It will be seen that for $c_3 = 0$ this ratio is zero, as it should be, and for c_3 infinite it is unity. Also, since the frequency appears in the ratio, the amplification will be different for different frequencies, so that the tube will distort and tend to eliminate higher frequencies.

With certain tubes and for certain frequencies for which the ratio $\mu/Rc_3 n$ is comparable with unity, the amplification is greatly impaired. This difficulty may, however, be avoided at any given frequency by the device of shunting the grid-plate capacity with an inductance of suitable value to make the impedance between grid and plate infinite at the given frequency. In doing this it is of course necessary to put in series with the inductance a large condenser to avoid conductive connection of grid and plate. It will be found that this method permits greater amplification at one frequency but it is open to the objection that variation of frequency is not convenient. Of course care must be taken not to couple this antiresonant mesh with others.

The Network as an Oscillation Generator.—In my PHYSICAL REVIEW paper the general theory of oscillation generators was given and it was shown that the possibility of sustained free oscillation of a network depends upon the existence of certain types of unsymmetrical terms in in the characteristic determinant. The vanishing of the determinant then determines both the frequencies of all the possible modes of free oscillation and also the relations which must hold among the circuit

constants in order that the oscillations shall be sustained (or have given damping). Since the solution for any oscillation generator requires only the ability to write down the network equations and find the roots of the determinant, it is hardly necessary to go into the detailed solution for any special case. As an example, however, the network of Fig. 5, purposely simplified to avoid long equations, will be handled by the method of the simplest equivalent circuit. The plate-grid capacity is

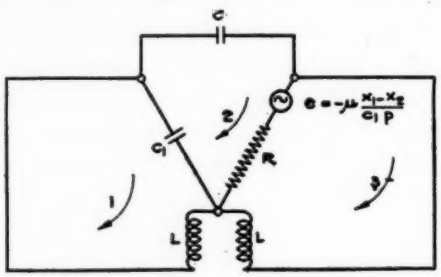

Fig. 5.

included in the capacity C and the mutual inductance of the two coils is m.

Choosing the mesh currents as shown, the network equations are

x_1	x_2	x_3	
$\frac{1}{c_1 p} + Lp$	$-\frac{1}{c_1 p}$	$-mp$	0
$-\frac{\mu + 1}{c_1 p}$	$\frac{\mu + 1}{c_1 p} + \frac{1}{Cp} + R$	$-R$	0
$mp + \frac{\mu}{c_1 p}$	$-R - \frac{\mu}{c_1 p}$	$Lp + R$	0

Note that these are the same as the last set with the addition of the transformer coupling. Now if we require that the oscillations be sustained, p must be taken equal to in, in which n is 2π times the frequency of oscillation. Then the vanishing of the determinant, which is complex, will require that the real and imaginary parts separately shall vanish, that is, that the even and odd powers of p shall separately be zero. As explained in the paper above cited, this determines both the frequencies of all the modes of oscillation and the circuit adjustments which must be made to permit the oscillations.

It will be noticed that in this determinant all the even powers of p appear in the coefficient of R; consequently by combining rows and columns until R appears in but one element, the even powers of p will be contained in the minor of that element, which minor, equated to

zero, will determine the frequencies of sustained oscillation. This process leads to the frequency equation:

$$(L^2 - m^2)p^4 + \left(\frac{L}{C} + 2\frac{L-m}{c_1}\right)p^2 + \frac{1}{Cc_1} = 0,$$

and there are therefore two possible frequencies of sustained oscillation, corresponding to the two values of $p^2 = -n^2$. Whether or not these oscillations will actually take place depends upon whether the circuit constants are adjusted to make the odd powers of p vanish. This second equation, obtained by equating to zero the imaginary part of $D = 0$, is:

$$(L^2 - m^2)\left(\frac{c_1}{C} + \mu + 1\right)p^2 + \frac{L + \mu m}{C} = 0.$$

If, when one of the values of p^2 obtained from the first equation is substituted in this, it is satisfied, the oscillation corresponding to that value of p will take place. This fact explains a peculiarity of this kind of circuit, namely the common experience that in changing the frequency of an oscillator circuit the frequency may suddenly jump to some entirely different value for a small change in the constants. The reason is that in the process of changing the frequency the circuit constants are so changed that the relation holding among them becomes more nearly correct for another oscillation which would not before satisfy that relation. For example, in circuits of the type above, the most stable frequency is, for most ordinary adjustments, approximately that determined by the transformer and condenser C alone; but for some relations of L, m, μ, etc., the circuit will not maintain this frequency but will pass to the other. It is possible to design a network in which, as a constant is varied, the frequency will jump discontinuously from one value to others. The converse problem is to design an oscillation circuit in which the condition for sustaining a given oscillation holds for all variations of the element which is used to vary the frequency. Such a circuit will be stable over the whole frequency range.

Returning to the particular circuit above, it will be seen that if the capacity c_1 is very small the frequency of sustained oscillation will be that for which

$$n^2 = \frac{1}{2(L-m)C},$$

namely that corresponding to the single resonant circuit of the transformer and condenser C. The second equation then shows that this oscillation will be sustained if $\mu = 1$. If the inductances of the two windings had not been taken equal, μ would have turned out to be a

function of L_1, L_2, m. It is worth noting that this circuit will oscillate even if there is no mutual inductance provided the circuit constants are properly adjusted. It then becomes identical with the amplifier, discussed above, with an inductive load.

It is probably unnecessary to mention the fact that the solution for all three-mesh oscillation generators may be derived directly from the determinant appropriate to this one by simply inserting the proper impedances. The solution for any case is theoretically just as simple, but practically the algebra is usually troublesome when there are more than three degrees of freedom. An exception is the case of so-called "iterative networks" which have periodic structures and certain other symmetrical networks.

As has been said, these methods of treating the audion in a circuit are approximate only, because of the limiting assumptions made, but considerable use of them in connection with experimental circuit work has shown that they are useful. The problem of finite amplitudes cannot be handled so generally, but when it is necessary to consider such refinements special methods are available which, it is hoped, may be given in another paper.

RESEARCH LABORATORIES OF THE
WESTERN ELECTRIC CO., INCORPORATED,
February, 1919.

THERMIONIC AND PHOTO-ELECTRIC PHENOMENA AT THE LOWEST ATTAINABLE PRESSURE.

By C. F. Hagenow.

Synopsis.—The object of these investigations was fourfold:

1. To study the photo-electric effect of tungsten at the lowest possible pressures, especially after the illuminated plate had been denuded of occluded gases by continued electronic bombardment of such energy as to maintain it at a white hot temperature.

The pressures attained were as low as 3.5×10^{-7} mm. of mercury. Upon denuding a tungsten plate of its occluded gases by raising it to a bright yellow heat by electronic bombardment, the photo-current rose to many times the value obtained before such denuding and further heating produced no further change.

2. To find, by direct observation, the short wave-length limit for tungsten and to observe how this changes, if at all, with the removal of occluded gases.

The upper wave-length limit of tungsten was located in the region between 2100 and 2300 Å. According to Einstein's equation, the corresponding values of the work necessary to free an electron from the metal would then be between 5.7 and 6.3 volts. These are larger than the corresponding values in the case of thermionic emission.

3. To observe, with the aid of the electric vacuum gauge, recently devised by O. E. Buckley, the progress of the clean-up effect, particularly at extremely low pressures.

Under the conditions employed it was not found possible to reduce the pressure by means of the clean-up alone lower than 10^{-5} mm., which was not as low as could be attained with the pump itself.

4. To study pressure and other changes accompanying the appearance of the "blue haze."

A gradually increasing potential difference was applied between the tungsten plate and a glowing filament until the blue haze appeared. *No pressure change whatever was observable at the moment of its appearance.* Certain current and voltage discontinuities, which occur under the experimental condition just described, were found to have characteristics similar to those observed by O. W. Richardson and Charles B. Bazzoni in the case of mercury vapor. The clean-up of the blue haze is very rapid and shows a striking increase in its rate of absorption as the pressure approaches the final minimum. This behavior is in marked contrast to the clean-up with a lighted filament, but without a field, and is quite similar to that observed by S. Brodetsky and B. Hodgson in their experiments with a vacuum tube discharge under the condition of abnormal cathode fall. At the pressures employed in these trials, about .01 mm. of mercury, this final pressure remained unchanged in the presence of the field, and did not change further even in those cases in which a trace of the blue glow remained in the tube.

I. EFFECTS OF ELECTRONIC BOMBARDMENT UPON PHOTO-CURRENTS FROM TUNGSTEN.

THE question of the part played by occluded gases in photo-electric phenomena has received the attention of many observers. Among those who have contended that the photo-electric effect is essentially dependent upon the presence of occluded gases may be mentioned Paech,[1] Fredenhagen,[2] Küstner[3] and Wiedemann and Hallwachs.[4] In particular, Küstner finds a total absence of the effect in the case of zinc when gases were removed. The zinc was scraped in vacuo and all "reacting" gases were removed by a spark discharge over potassium.

These conclusions are contradicted by experiments made by Pohl and Pringsheim,[5] Hennings,[6] Piersol,[7] Dushman,[8] Millikan and Souder,[9] and Welo.[10] For example, Piersol finds an increased sensitiveness in a number of metals when the occluded gases are removed by heating the electrode with an electric current. He also observed a superposed maximum effect "dependent on the activity of the gaseous surface," which disappeared after the highest temperature was reached.

This author states that a vacuum of .0002 cm. of mercury was used

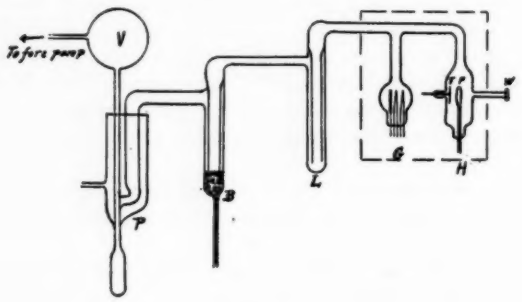

Fig. 1.

and does not mention the use of liquid air, so that the degree of exhaustion which he attained was not of the order aimed at in this experiment.

As the technique for the removal of the occluded gases and production of higher vacua has been improved, the evidence has become more and

[1] G. Paech, Ann. der Phys., 43, 135, 1913.
[2] K. Fredenhagen, Phys. Zeit., 15, 65, 1914.
[3] H. Küstner, Phys. Zeit., 15, 68, 1914.
[4] G. Wiedemann and W. Hallwachs, Ber. d. D. Phys. Ges., 16, 107, 1914.
[5] R. Pohl and P. Pringsheim, Ver. d. D. Phys. Ges., 16, 336, 1914.
[6] A. E. Hennings, PHYS. REV., 4, 228, 1914.
[7] R. J. Piersol, PHYS. REV., 8, 238, 1916.
[8] See I. Langmuir, Phys. Zeit., 15, 524, 1914.
[9] R. A. Millikan and W. H. Souder, Proc. Nat. Acad. Sci., 2, 19, 1916.
[10] L. A. Welo, PHYS. REV., 4, 251, 1918.

more conclusive for the contention that the photo-electric effect is an intrinsic property of the pure metal. This paper furnishes further convincing support of this point of view.

The apparatus (Fig. 1) was exhausted by the mercury diffusion pump P (kindly furnished by the Western Electric Company), working against a fore-vacuum of .01 mm. of mercury, or less, produced by a Töpler pump. Once established, no further pumping was necessary, as the volume, V, was quite large compared with that of the rest of the apparatus. A barometer tube, B, served as a valve to shut off the part to the right of it. L is the liquid air trap, which was kept continually in liquid air while the apparatus was set up. At no time was there any evidence of mercury vapor in the tube H. For measuring the pressures the extremely sensitive ionization gauge, G, due to Buckley,[1] was used. The photo-electric tube, H, contained the tungsten plate,[2] T, opposite which, at a distance of about a centimeter, the tungsten filament, F, and, in line with both, a tube sealed with a quartz window, W; the last being fastened with De Khotinsky wax. The connecting tubing had a bore of about 2.5 cm. and the whole apparatus was made as compact as possible. The source of illumination was, for the most part, a spark between zinc terminals. To avoid all electromagnetic disturbances, the spark gap, together with the induction coil, storage cell and Leyden jar, were all enclosed in an iron box.[3] A Dolazelek electrometer served for measuring the photo-currents, a sensibility of about 300 mm. per volt being usually employed. An electric oven could be slipped over a region indicated in the figure by the dotted line.

The ionization gauge, calibrated by Buckley against both a McLeod and a Knudsen manometer, gives the pressure in millimeters of mercury according to the formula (for air),

$$p = .05 \frac{I_C}{I_A},$$

where I_A is the current, in amperes, set up by a coated filament in a field of 200 volts and I_C the resulting flow of positive ions. The former can be read on a milli-ammeter, at least for the larger values, and the latter by means of a galvanometer. In order to read the smaller currents for I_A at the higher pressures more accurately, the writer employed the following null method of measuring these small currents. Fig. 2 shows the connections. A known resistance, R_1 is placed in series with the

[1] O. E. Buckley, Nat. Acad. Sci. Proc., 2, 683, 1916.

[2] This was a thorium free sample kindly furnished by Dr. Langmuir and of the same sort used by him in the determination of Richardson's "b."

[3] W. H. Kadesch, PHYS. REV., 3, 367, 1914.

circuit whose current it is desired to measure. Connected to one end, A, of this resistance, is a circuit containing a variable resistance, $R_2 + R_3$ and a cell, whose E.M.F. need be known only to the degree of accuracy of the gauge itself. A Leeds and Northrup portable galvanometer was put at G. The adjustment consists simply in finding a point B' so that on closing the key, K, no deflection resulted. B and B' being then at the same potential, we have, calling the currents in R_1 and R_2 respectively C_1 and C_2,

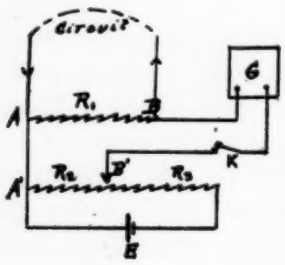

Fig. 2.

$$C_1R_1 = C_2R_2.$$

Also

$$C_2 = \frac{E}{R_2 + R_3},$$

Therefore

$$C_1 = \frac{R_2E}{R_1(R_2 + R_3)}.$$

As actually used, the resistances were set in a fixed relation and the heating current of the glower of the gauge regulated for zero deflection of the galvanometer. Since I_A need not be changed very often (*i. e.*, only for a large variation in the range of pressure) a few previously calculated values of R_1, R_2 and R_3 enabled one quickly to set on any desired current.

The limit of this instrument to indicate low pressures is set only by the possibility of being able to measure the current I_C. On the other hand, it was found that a maximum reading was obtained at .019 mm. This was located by plotting the values of I_C against time as the apparatus was gradually exhausted by a Gaede mercury pump.

The photo-currents measured were the saturation currents for a timed duration of the spark. The plate T (Fig. 1) was connected to one of the quadrants of the electrometer, the other being earthed. A positive potential was applied to the filament, F, the other pole being earthed, and the liberated electrons thus removed from the tube. A field of 10 to 20 volts was sufficient for saturation.

With the apparatus as first set up and no further exhaustion than simply pumping with the diffusion pump, the following readings were taken.

The photo-currents are expressed in millimeters deflection on the basis of 300 mm. per volt sensibility and 2-second illumination when the electrometer alone is used. (Sometimes an auxiliary condenser had to be connected.) These are given under C in the last column.

TABLE I.

Date.	No.	p.	C.	Date.	No.	p.	C.
May 10	1	4.8×10^{-3}	9.6	May 13	8	7.7×10^{-3}	9.8
11	2	"	7.2	14	9	5.2×10^{-3}	8.7
12	3	"	7.1	"	10	3.8×10^{-4}	7.7
"	4	"	6–6.8	"	11	1.4×10^{-4}	8.1
"	5	"	8.2	"	12	8.0×10^{-5}	8.9
13	6	5.0×10^{-3}	7.9	15	13	5.1×10^{-5}	7.8
"	7	3.2×10^{-4}	8.7	"	14	8.5×10^{-5}	7.3

As is to be expected from all preceding photo-electric work there is here no evidence for a relation between pressure and photo-currents. The table includes every run that was made until the apparatus was opened. On one or two occasions the writer has noticed fluctuations in excess of those here recorded, but the foregoing are representative of the sort of constancy that readings, taken days or weeks apart under apparently the same conditions, would show.

It may be mentioned, parenthetically, that readings were sometimes taken at zero fields, the filament F being earthed. Both T and F being of the same metal there should be no contact potential present. The results were very variable in this case as might be expected under the conditions. The number of electrons caught by the filament would depend on their particular distribution at any particular time, and this would be influenced by the charging of the inner surface of the glass tube. It was observed that illuminating the plate repeatedly, even when it was earthed at the time, would cut down the ensuing current greatly, doubtless because of such accumulation of charge on the walls. The effect would disappear after a short while. This phenomenon practically ceased at the saturation voltage, as it should do if the foregoing explanation is correct.

The effect upon the photo-currents, C, of denuding the tungsten plate of gases is shown in Table II. The headings have the same significance as in Table I. The denuding was done by glowing the filament while the negative potential indicated in the last column was applied to it.

So far no parts of the apparatus had been baked out or the metal parts heated, except the illuminated plate as described.[1]

No further readings were taken for four months. A new tungsten plate was mounted, though from the same original piece. Then the data contained in Table III. were taken.

The increase in no. 3 is not as large was as expected in view of the

[1] The ionization gauge and the tungsten filament in the photo-tube had been renewed since the readings in Table I. were taken.

TABLE II.

Date.	No.	p.	C.	Remarks.
June 9	1	1.5×10^{-3}	1.4	Just after set up.
"	2	"	187.6	After first bombardment, for 10 minutes up to 960 volts D.C. No observable heating of the plate.
11	3	1.9×10^{-3}	133.0	No further treatment since last observation.
12	4	2.0×10^{-3}	433.0	After bombardment with 1,500 volts, about 30 minutes.
13	5	1.9×10^{-3}	449.0	No further treatment since last observation.
		(Apparatus opened.)		
July 6	6	2.6×10^{-3}	94.0	Note decrease after exposure to the air.
"	7	2.0×10^{-3}	1885.0	After bombarding at 1,500 volts. Not visibly heated but surface slightly altered in appearance.
"	8	2.0×10^{-5}	1900.0	After pumping down to 1/100 value of preceding pressure. Practically no effect on the photo-current.
7	9	1.6×10^{-3}	1715.0	Day after a bombardment up to 1,400 volts, about 30 minutes. First time plate at red heat in spots.
		(Apparatus opened.)		
18	10	2.9×10^{-3}	4.0	Decrease after exposure to air.
"	11	4.8×10^{-4}	968.0	After bombardment at 3,500 volts A.C. about 30 minutes. Plate bright red in central portion, duller at edges.

effect of other cases of bombardment. Also the spontaneous increase in no. 6 is hard to account for, unless the fact mentioned in the last column may have had some bearing on it. However in view of the results of all these observations, it appears that there is an enormous increase of photo-sensitiveness after the occluded gases are removed. No. 7 shows the final reading at the lowest pressure attained for photo-electric observations in the course of these experiments. The tube and guage had been baked out, the metal parts all glowed (the collector plate of the gauge had shown no visible heat during the bombardment, but a subsequent bombardment that caused it to glow did not influence the pressure attained). It can then fairly represent the conditions of a pure metal in a very low pressure thoroughly out-gassed. The close agreement of the final values of C in Tables II. and III. is probably largely accidental. On account of a rearrangement of the set up, necessitated by the addition of a monochromatic illuminator, the intensity of illumination of the plate in Table III. was slightly changed.

According to Table II. the maximum photo-current occurs after only

TABLE III.

Date.	No.	p.	C.	Remarks.
Nov. 30	1	2.2×10^{-3}	50	
Dec. 1	2	"	93	After a slight bombardment to try a new transformer.
Jan. 1	3	6.2×10^{-5}	112	After bombarding 15 minutes at 3,500 volts A.C. Plate at red heat all over.
2	4	9.0×10^{-4}	106	No further treatment since last observation.
3	5	1.1×10^{-5}	111	After baking tube and gauge for one hour at 300° C.
7	6	1.2×10^{-4}	407	This was after the tungsten filament had been brightly glowed for one hour for a clean up experiment.
8	7	3.5×10^{-6}	964	After bombarding 15 minutes at 2,200 volts A.C. Plate at a bright orange yellow heat. Now appears for the first time a bright metallic lustre.

a moderate heating of the plate. This maximum does not appear in Table III. and is probably due to some accidental surface condition in the first case. Piersol,[1] however, has observed a similar phenomenon in the case of a number of other metals. When new trials along this line were undertaken some weeks later, troubles unfortunately developed with the mountings of the tungsten plate that made further tests of this kind impossible.

Pressure readings were made with this apparatus down to 3.5×10^{-7} mm., with the photo-tube taken off. This is below the lowest pressure which it was possible to maintain for photo-electric observations. The De Khotinsky wax, used to hold the quartz window, may account for this difference. Also, as has been mentioned above, it was impossible to bake out every part of the apparatus. An attempt to heat the parts not inclosed by the oven with a Bunsen burner, while the diffusion pump was in operation, proved a failure. With the gauge and tube in the electric oven, and the diffusion pump going, mercury vapor diffused over into the tube.

It was also found that, though taking off the liquid air caused the pressure to rise rapidly, the vacuum could be as quickly restored by replacing it, with the pump in operation. Thus in one case the pressure rose almost immediately from 5×10^{-6} to 1.2×10^{-2} mm. and returned to 5×10^{-6} mm. It may be remarked that the low pressures mentioned just above were read after mercury vapor had diffused through the tubing as described.

[1] *Loc. cit.*

II. DIRECT OBSERVATION OF LONG WAVE-LENGTH LIMIT OF TUNGSTEN.

To determine the long wave-length limit of sensitivity of the tungsten a Hilger monochromatic illuminator was set up before the quartz window; a Heræus quartz mercury lamp being the source of light. As used with this apparatus, this lamp with direct illumination of the tungsten plate, gave a scale deflection about three times as large as that obtained previously with the zinc spark, *i. e.*, about 1,000 mm. in two seconds of illumination when no condenser was used. When the light was passed through the monochromator it was found impossible to obtain any deflection at all with any wave-length which would pass through the instrument. However some idea was gained of the limits of sensitiveness by means of two absorption media.

A solution of methyl alcohol placed in the path of the direct beam from the source[1] cut out the effect entirely. The first trials were made after the runs no. 2 in Table III. Other trials after no. 3 gave the same results. Finally after the last run, no. 7, a small deflection was observed. This was less than one thirteen hundredth of the deflection caused by the unfiltered light and about twice that which could still be observed with certainty. Since this sensitiveness was not attainable before the plate was thoroughly out-gassed, any conclusions as to a real change of the wave-length limit based on the absence of any observable effect under those conditions would be correspondingly doubtful.

The empty absorption cell itself, by virtue of the absorption of its fused quartz windows, cut down the deflection to only one tenth of its value, both before and after the plate was out-gassed.

Mt. M. J. Kelly, at this laboratory, found, photographically, that methyl alcohol had a sharply defined absorption region beginning with decreasing wave-length, at 2370 Å, and that the fused quartz windows had a similar absorption region beginning at 2160 Å. Now the above experiment showed that about nine tenths of the total light effect must have been due to wave-lengths shorter than 2160 Å, and all but one part in thirteen hundred to wave-lengths less than 2370 Å. The question arises whether this residual effect is due to active wave-lengths longer than 2370 Å or to a very small amount of light of shorter wave-length that was not entirely absorbed by the methyl alcohol. The latter is the more natural assumption, so that the indication of this experiment is that the long wave-length limit of tungsten is between 2100 and 2300 Å.

We can compare these results with the minimum frequency for which tungsten is light-sensitive, as calculated from Einstein's equation,

$$h\nu_0 = w_0$$

[1] The zinc spark was also used at times.

where w_0 is the work done by an escaping electron against the forces which tend to retain it in the metal. If we assume that w_0 has the same value as in thermionic emission, we can use its value as obtained from thermionic experiments. Lester[1] has made some experimental verifications of the identity of the "work function," φ, of an electron escaping from a metal and "b" in Richardson's equation,

$$i = a\theta^{1/2}e^{-b/\theta}.$$

The relation is

$$\varphi e = bk,$$

where e is the charge on an electron, k the gas constant for one molecule. φ was calculated from experiments made on the "cooling effect." Now if we assume that w_0 in Einstein's equation has the same value as in thermionic emission, using Lester's value for tungsten, $\varphi = 4.478$ volts, we have

$$\nu_0 = \frac{\varphi e}{h} = \frac{4.478 \times 4.774 \times 10^{-10}}{300 \times 6.547 \times 10^{-27}} = 1.088 \times 10^{15},$$

or

$$\lambda_0 = 2757\text{Å}.$$

On the assumption that the experiment with the methyl alcohol light filter does really indicate a total absence of light sensitiveness to wave-lengths longer than 2370 Å, the difference is seen to be at least 400 Å. This is much larger than the variations in either the values of φ as observed by Lester, or the values of b obtained by Langmuir when proper precautions were taken to have all occluded gases removed.

It may be mentioned that Lester's value of b $(= \varphi e/k)$ is 52,130. This agrees well with the weighted mean value, $b = 53{,}130$, which that writer has calculated from some measurements by Smith[2] and Langmuir.[3]

Lester[4] also found that the effect of residual gases was to increase the value of φ. This he tested by sealing off a tube containing a tungsten filament and allowing the glowing filament[5] to clean up the active gases present. Inert gases do not affect φ. If this fact has any direct bearing on the present experiment it would mean that the occluded gases responsible for the higher value of φ were such that they were not driven out by the treatment the plate received as described above.

It is, of course, not established that the work function is the same in photo-electric as in thermionic emission, or that these phenomena deal with the same type of electron. Concerning the case of platinum

[1] Horace Lester, Phil. Mag., 31, 197, 1916.

[2] K. K. Smith, Phil. Mag., 29, 802, 1915.

[3] I. Langmuir, Phys. Rev., 2, 450, 1913.

[4] *Loc. cit.*

[5] *I. e.*, the same filament which was the subject of investigation.

Hughes[1] makes the following comparison: Richardson[2] gives 5.34 volts as representing the work done (per unit charge) when an electron escapes from hot platinum. But from photo-electric observations, using the most probable value of λ_0, viz., 2910 Å, V_0 comes out 3.86 when calculated from $V = kv - V_0$. When instead of k the corresponding value from the quantum theory, h/e is used, V_0 becomes equal to 4.32 volts.

The results of the present experiments indicate a value of the work function, calculated from Einstein's equation, as lying between 5.7 and 6.3 volts. The work required to remove an electron from tungsten photo-electrically thus seems to be larger than that required in the case of thermionic emission.

III. Clean-up Effects.

The fact that an incandescent filament tends to improve the vacuum has been noted by many observers. It has been subjected to detailed study by Langmuir[3] for a number of gases.

The present attempt offers nothing new, except as it might serve to make a comparison with another sort of clean-up to be discussed later in connection with the blue haze experiments.

The mercury valve, B (Fig. 1), was closed and the filament glowed a little more brightly than in the ordinary Mazda lamp. The following readings were then taken.

Table IV.

Time (Minutes).	p.	Absorption Cu. mm. $\times 10^{3}v$.	Per Minute.
0	1.2×10^{-4}		
5	6.8×10^{-5}	6.84	1.37
10	3.5×10^{-5}	4.55	.91
20	1.9×10^{-5}	2.20	.22
30	1.6×10^{-5}	.40	.04
40	1.4×10^{-5}	.26	.026
50	1.3×10^{-5}	.13	.013
60	1.25×10^{-5}	.07	.007

The absorbed air is given in cu. mm. at atmospheric pressure per cu. mm. of the volume, v, of the apparatus used. The last column contains the average rate per minute in the same units.

The next day but one following this run the pressure was found to have risen to 2.8×10^{-5} mm., when the filament was again glowed at a higher temperature, bringing the pressure down to a little below 10^{-5} mm. The graph is shown in Fig. 3.

[1] A. L. Hughes, Photo-electricity, Cambridge University Press.

[2] O. W. Richardson and K. T. Compton, Phil. Mag., 24, 576, 1912.

[3] I. Langmuir, J. Am. Chem. Soc., 34, 1310, 1912; 35, 107, 1913; 35, 931, 1913.

Table IV. shows that the rate of clean-up, as shown in the last column, diminishes to 1/200th of its initial value while the pressure drops to 1/10th of its original amount. According to Langmuir[1] the rate of clean up for oxygen is proportional to the pressure. For nitrogen[2] it is different according to the range of pressure experimented with, but is in-

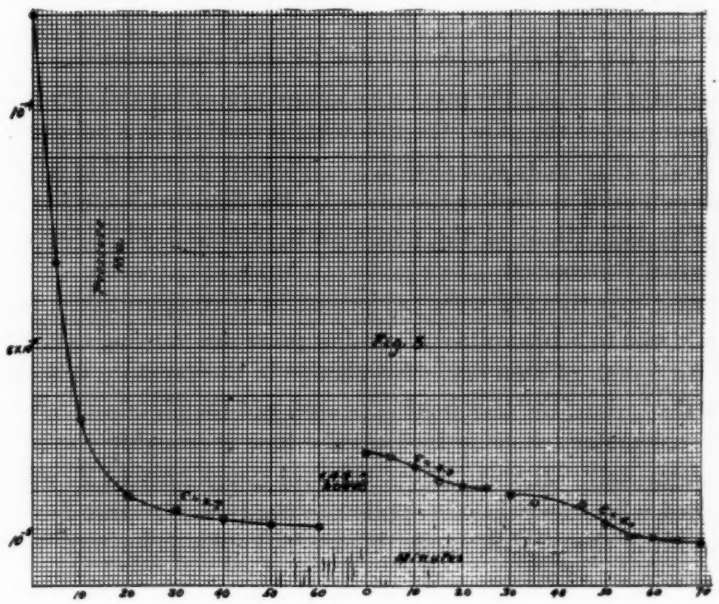

Fig. 3.

dependent of the pressure in the interval from .0065 mm. to .0001 mm. of mercury.

The present experiment indicates that the rate of clean up of air decreases at a greater rate than the pressure and that the latter reaches a fairly well defined limiting value, which is manifestly not due alone to the inert gases. Langmuir found a "fatigue effect" in the case of hydrogen, so that a continual treatment of the glowing wire in that gas brought the clean-up practically to a standstill. In view of these experiments and the fact that the rate of clean up depends on the temperature of the filament in a way widely different for the different gases, no general conclusions can be drawn from experiments on a mixture such as air.

IV. Phenomena Accompanying the Appearance of the "Blue Haze."

The bluish glow, known as the "blue haze" has often been remarked.[3]

[1] I. Langmuir, J. Am. Chem. Soc., 35, 107, 1913.

[2] *Loc. cit.*, 35, 931, 1913.

[3] W. R. Whitney, Proc. Am. Inst. El. Eng., 31, No. 1, 921, 1912. Saul Dushman, PHYS.

It can be seen, at a certain state of exhaustion, in the ordinary incandescent lamp. Whitney[1] observed that it "cleaned up" gases and was accompanied by a disintegration of the lighted filament.

The present investigation may be grouped under three heads: (A) Pressure changes and general observations; (B) Current-voltage relations; (C) Clean-up effects.

(A) *Pressure Changes and General Observations.*

To attempt to study the pressure changes preceding and accompanying the appearance of the glow, the following procedure was adopted.

The valve B (Fig. 1) was closed, the filament F glowed brightly and a positive potential applied to the plate T; the filament being the negative pole. The indications of the gauge were observed while the potential was gradually increased.

The first experiments were performed at a comparatively high field voltage of 900 to 2,100 volts A.C. and at pressures varying from 6×10^{-4} to 5×10^{-5} mm. of mercury. No change in the pressure was observed, even at the instant the blue haze appeared and the plate was red hot with the bombardment (showing incidentally how thoroughly the metal had been out-gassed). It was noticed that the gauge current I_A was always diminished when the field was applied to the tube H. But I_C was found to diminish in the same ratio, so that as far as the gauge indicated, there was no change of pressure.

In order to bring the necessary potential within lower and more accurately measurable limits, it was decided to use a pressure as high as .01 mm. A potentiometer supplied the field up to the available 220 volts, D.C.

It was then observed that the blue haze appeared very sharply, accompanied by a sudden fluctuation in the voltage downward and a break upward in the electronic current. This phenomenon has been described by Richardson and Bazzoni,[2] in their experiments on mercury vapor.

At the first one of such fluctuations a blue glow appears directly behind the anode; it can be made to appear and disappear within a variation of potential too small to be observed on a Weston 30-volt voltmeter, with which a change of one fifth volt could be easily detected. On increasing the field the glow spreads into the tube and, a little later, at a voltage which seemed to be constant for all pressures tried, a second "kick" occurred. Here the glow suddenly spread further into the tubing above

REV., 4, 123, 1914. A. Wehnelt and E. Liebreich, Phys. Zeit., 15, 557, 1915. O. W. Richardson and Charles B. Bazzoni, Phil. Mag., 32, 426, 1916.

[1] *Loc. cit.*

[2] *Loc. cit.*

the bulb H and also increased greatly in intensity. At this point the glow was very sharply defined and a column of it could be pushed along the tubing at will by controlling the field.

The gauge showed no change in the pressure at any time, except that after some minutes it would begin to register the falling pressure due to the above-mentioned clean-up effect. The blue glow then began gradually to recede into the tube H and finally to disappear altogether. The rate of disappearance depends on the pressure of the absorbable gases present, and for the lower pressure, the rapid disappearance of the glow, once it begins to withdraw, is very striking. As shown at the end of the paper, this disappearance was accomplished at times in an interval of a second. In these experiments also, as in the first trials with A.C. fields, it was observed that the gauge current I_A was always diminished when the field was applied in the tube H. But I_C diminished in the same ratio, so that the gauge recorded no change in pressure.

(B) *Current-Voltage Relations.*

In order to maintain the pressure as nearly constant as possible during a set of observations the mercury seal B was left open. A constant P.D. of seven volts was maintained across the terminals of the filament. To the apparatus mentioned above was added a milliammeter. A typical set of readings is shown in Table V. V_1 is the first "kick" voltage, when the blue color first appears behind the anode; C_1 the corresponding current change. In this set the initial current was not readable on the scale used. V_2 is the voltage drop at the second kick, already referred to above. The voltages are measured at the positive end of the glowing filament, the average would thus be 3.5 volts greater. Under C_2 are given the current readings corresponding to the voltages, V_2.

TABLE V.

No.	p.	V_1.	C_1.	V_2.	C_2.
1	.0101	18 → 14	0 → .005	26 → 22	.130 → .133
				30 → 25	.135 → .140
2	.0086	22 → 16	→ .006	22 → 20	.113 → .115
3	.0068	24 → 16	→ .007	22 → 20	.118 → .122
4	.0047	33 → 18	→ .013	25 →	
5	.0023	54 → 24	→ .026		
6	.0010	92 → 44	→ .045		

Owing to the fact that even with the considerable volume in use the pressure would slowly diminish, it was usually impossible to duplicate any reading during a run. The kicks are rather hard to catch accurately

and rapid fluctuations are apt to occur at these points of instability, especially at the lower pressures. Thus in case of no. 6 the voltage and current made the jump back and forth twice, finally remaining at the "before the kick" value. This meant, of course, that the clean-up had progressed so far that the higher potential of V_1 was not sufficient to start the blue glow again.

Fig. 4 is the plot from the above data. No. 1 seems to have three points of instability, though that may well be the result of the manipulation of the potentiometer. It did not occur in the other sets. The

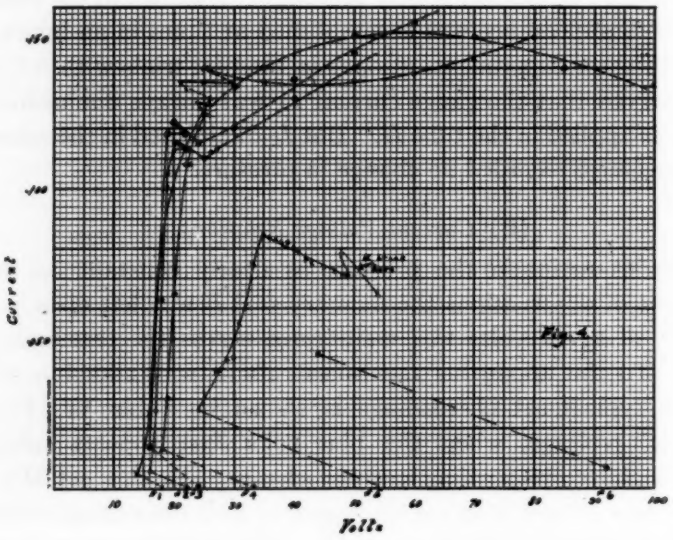

Fig. 4.

currents before the first break are not shown in the plot; they increase gradually from zero until the break. Thus the whole phenomenon resembles that described by Richardson and Bazzoni[1] in the case of mercury, even to the order of magnitudes involved. These observers mention also the second point of instability, but are of the opinion that it is due to the "discharge wandering in the tube" and did not regard it as of as much interest as the first. Coming as it does at approximately the same voltage for all the pressures would suggest that it is a function of the apparatus rather than of the other conditions. This would remain to be investigated.

Referring again to the curves, it seems as if in no. 5 the first break had overtaken the second, being just at that voltage; it shows also another break later. But the conditions at that stage were too variable to make

[1] *Loc. cit.*

any general statement. This is also evident from an inspection of the progress of the currents, after the first very rapid increase immediately after the first break. No. 6 consisted of only the first jump.

A second table is added to show the duplicability of the phenomenon. The seventh column gives the ratio of the currents, before and after the first kick. This was used by Richardson and Bazzoni as a measure of the magnitude of the kick. It shows a maximum as found by them.

TABLE VI.

No.	p.	V_1.	$C_1 \times 10^4$.	V_2.	C_2.	Ratio of C_1's.
1	.0120	17 → 14.5	.75 → 5.9	26 → 24	.104 → .107	7.9
2	.0113	19 → 16	1.5 → 12.0	28 → 22	.136 → .148	8.0
3	.0070	26 → 16	1.8 → 40.0	22 → 21	.105 → .108	22.2
4	.0026	60 → 26	2.7 → 50.0	28 → 26		18.5
5	.0013	114 → 42	45 → 600			13.3
6	.0009	206 → 105	110 → 1270			11.5

The behavior of the voltage V_1, also, is similar to that found by those observers for mercury. Thus, an attempt to lower the voltage after the first "kick" results in a sudden drop to the initial part of the curve; *i. e.*, to a smaller current and larger voltage.

As is evident from Tables V. and VI., the minimum potential necessary to maintain the glow (which is practically the lower reading in the column under V_1) approaches a limiting value as the pressure increases. In these experiments the minimum value for V_1 was never below 14 volts, with a pressure up to .02 mm., the highest readable on the gauge. Taking account of the potential difference across the terminal of the glowing filament, the average potential would be 17.5 volts. Compared to the ionizing potential for nitrogen (using 7.7 volts), this is roughly in the same ratio as the corresponding quantities Richardson and Bazzoni found for mercury, viz., 11.5 volts for the glow as compared to minimum ionizing potential of 4.9 volts. However, in the light of some recent experiments by Hebb,[1] who has shown that pure mercury vapor will arc at 4.9 volts, the above comparison may not have any significance. The present trials were necessarily complicated by the fact that they were made on a mixture of gases subject to a sorting-out effect due to the clean-up. A detailed study of this phase of the ionization problem on pure gases would seem to be a profitable undertaking.

The writer does not lose sight of the fact that where there is very probably a selective absorption of the gases present in air, the gauge constant would be subject to change. Nevertheless, such a variation

[1] T. C. Hebb, PHYS. REV., 11, 170, 1918.

would not obliterate the general trend of the phenomenon in question. This also applies to the experiments on clean-up effects, which follow.

(C) *Clean-Up Effects.*

The clean-up effect of the blue haze was very marked, as was the wearing away of the lighted filament. The walls of the tube became covered with a shiny brown coating, showing interference colors. Langmuir[1] refers to a "clear brown" coating as being WN_2. This clean-up is characteristically different from that produced by the lighted filament without a field between the filament and a neighboring electrode. As will be shown more in detail later, the rate of clean up is quite different and increases with decreasing pressure just before the blue glow disappears. Also it operates at a considerably higher pressure than the ordinary clean-up. Thus it was always possible to evacuate with the blue haze at .02 mm. pressure, though a glowing filament, without the field, had absolutely no effect at this pressure.

In order to accelerate the progress of the phenomenon a smaller volume was used, B being closed. The first observations were taken immediately after the experiments described in part "B" above were completed; that is, after the air in the apparatus had presumably been deprived of its more easily absorbed constituents.

The filament being glowed as before and the maximum field applied (not over 220 volts) pressure readings were taken at intervals of a minute, during the first two runs. As soon as the minimum pressure was attained, B was opened a moment, thus equalizing the pressure throughout the apparatus, and B again closed for the next run.

The tube and about half of the connecting tube to the gauge was filled with intense purple glow which turned to a pure blue as the exhaustion proceeded. After a time the glow would begin to recede into the tube and, usually, disappear altogether. In the instances where a glow remained there was no difference in the pressure observed. The rapid decrease in the time required for glow to disappear as run after run was made was very striking. Table VII. gives a summary of these trials. The initial and final pressures are denoted by p_1 and p_2 respectively; t is the time taken for the glow to disappear, which was also the interval between the two pressure readings, as nearly as they could be taken. No great accuracy is claimed for the time in the shorter intervals, but they serve sufficiently to indicate the progress of the phenomenon. The quantities in the last two columns are the same as the corresponding ones in Table IV.

[1] I. Langmuir, J. Am. Chem. Soc., 35, 931, 1913.

TABLE VII.

No.	p_1.	p_2.	t, Seconds.	Absorption Cu. mm. $\times 10^6 v$.	Absorption Per Min.
1	.0110	.0015	360	12.5	2.10
2	.0076	.0011	240	8.55	2.14
3	.0072	.0010	30	8.16	16.3
4	.0065	.0009	20	7.37	22.1
5	.0062	.0015	4	6.2	93
6	.0058	.00061	2	6.8	205
7	.0053	.00068	1	6.0	360
8	.0049	.00099	—	5.4	—
9	.0046	.0011	—	4.6	—

Thus as the proportion of absorbable gases decreases with each run, the rate of clean-up increases. The total pressure at the beginning of the final run is only a little less than half that at the commencement of the experiment.

The matter was next tested by admitting a fresh lot of air into the apparatus. The valve B was left open and the entire apparatus evacuated in the above manner. Readings were taken every minute or two until a steady state was reached at a pressure of .0008 mm. at the end of 45 minutes.

The results are best represented in a graph, shown in Fig. 5. The

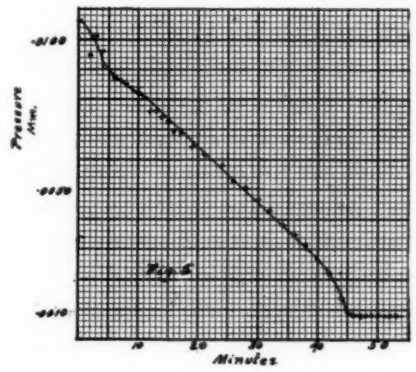

Fig. 5.

curve is practically a straight line up to a pressure of .0022 mm., when there is a rapidly increasing acceleration until the minimum pressure is attained. It is at that point the glow begins to recede and disappear.

The field and current strength were recorded. Both remained at a fairly steady state during the greater part of the time, *i. e.*, until the bend in the curve was reached, when the voltage rose and the current fell rapidly.

In the present case we are dealing with a mixture of gases, hence, since the rate of absorption increases with the diminution of the total pressure, it must vary still more rapidly with the partial pressure of the more absorbable constituents.

According to Langmuir[1] the oxygen atoms collide with electrons in the tungsten filament by virtue of the energy of agitation of the former, which then take on a negative charge and combine with positive tungsten atoms. A field might conceivably aid or retard this process; negative oxygen ions being repelled before chemical combination could take place; or, positive ions of the gas impelled to the negative filament.

In an investigation on the absorption of gases in vacuum tubes, Brodetsky and Hodgson[2] have given evidence for a mechanical theory of the phenomenon. Glass vacuum tubes were used, the current being obtained from a high potential battery. A curve for air shown by them has the general characteristics of Fig. 5.

According to their work the absorption, together with the disintegration of the cathode, is conditioned on the presence of an abnormal cathode fall: neither of the two effects appearing when the cathode fall is normal. The fact is cited (supporting the mechanical theory) that the inactive gases helium and argon are also readily absorbed. Hodgson[3] shows curves, similar to the above, for helium. Whatever may be the mechanism of the process, the absorption in the case of the blue haze is certainly of the same nature as the vacuum tube discharge. Just how selective it is and how it may vary with the field, which affects the ionization, remains a subject for further investigation. In all cases of absorption with the blue haze in the present experiments the minimum pressure was about 10 per cent. of the initial one. This is of course too large to be accounted for by a residue of the inert gases alone.

A number of attempts were made to obtain some information of the nature of the process by spectroscopic means.

A Schmidt and Haensch direct vision spectrometer (after Hoffmann) was employed. As has been stated above, the color of the glow changes from a sort of purple to a pure blue toward the end of the exhaustion. The spectrum of the blue haze at .01 mm. pressure showed the brighter nitrogen and oxygen lines and some of the nitrogen bands of the first and second Deslandres series as described by Kayser. No hydrogen lines were seen. After a clean-up, whenever there remained a visible glow, it was found that the nitrogen bands of the first group had disappeared and some of the second. H_α and H_β were observed.

[1] I. Langmuir, J. Am. Chem. Soc., 35, 107, 1913.

[2] S. Brodetsky and B. Hodgson, Phil. Mag., 31, 478, 1916.

[3] B. Hodgson, Phys. Zeit., 13, 595, 1912.

It was thought that the removal of a great deal of the nitrogen and oxygen might allow other lines to become more prominent, such as those of argon. In order to make possible a more careful and detailed study of the spectrum, a table was constructed showing the observed lines and the most prominent lines of the common and the noble gases in parallel columns. A number of new lines did appear that corresponded to those of argon within the limits of accuracy of the spectroscope, but they were not among the prominent ones, and could usually be duplicated by either nitrogen or oxygen, though these latter had not been seen before the clean-up. Thus it was practically impossible to draw any safe conclusions from the character of the spectrum. Also the feeble luminosity, in the bright glare of the lighted filament, made observation difficult.

In conclusion the writer wishes to take this opportunity to thank Dr. Millikan, at whose suggestion these experiments were undertaken, for his very kind assistance and numerous helpful suggestions.

RESIDUAL GASES AND VAPORS IN HIGHLY EXHAUSTED GLASS BULBS.

BY J. E. SHRADER.

SYNOPSIS.—The investigation of high vacua has been extended by making observations on the effect of the sealing off of highly exhausted glass bulbs, and noting the subsequent change in pressure with time over an extended period. On sealing off the bulbs and gauges by melting the glass at a constriction there is a comparatively large evolution of gases and vapors which can be partly removed by pumping during the time of sealing off, but the pressure in the bulbs is always four or five times as large as the pressure before sealing off.

BY the use of the mercury diffusion pump and the Knudsen absolute gauge pressures of the order of 1×10^{-8} mm. Hg have been produced and measured.[1] These pressures have been measured during the operation of the pump and it has not come to the attention of the author that any data have been obtained showing what pressures can be maintained in bulbs which have been pumped to this degree of exhaustion and sealed off. To secure information on this subject four glass vessels were exhausted to a high vacuum and sealed off and their change in pressure with time was observed. The system for this investigation consisted of a mercury diffusion pump with liquid air trap, a sensitive Knudsen absolute gauge of about 500-c.c. capacity and the bulb to be tested of about 1,500-c.c. capacity. A narrow constriction was made in the tube connecting the bulb and gauge to the pump so that they could be sealed off readily by heating a limited amount of glass. The gauge and bulb were so disposed that they could be heated by an electric oven to a short distance beyond the constriction. At the same time all the glass connecting tubing was heated with a bunsen flame to release occluded gases and vapors.

It has been recognized that the vacuum obtainable with the diffusion pump is limited practically by the heat treatment of the glass, though it is true that the greater the speed of the pump the lower the pressure that can be reached. Equilibrium will be established when the speed of the pump is equal to the rate at which gases and vapors are given off from the glass. If the escape of the gases and vapors is accelerated by

[1] Shrader and Sherwood, Production and Measurement of High Vacua. PHYS. REV., Vol. XII., No. 1, July, 1918.

heat treatment, this equilibrium is reached sooner and the ultimate pressure is lower. The effect of heat treatment on the vacuum obtainable after pumping until equilibrium was reached at that temperature is shown by the following results:

Temperature.....	20	100	200	300	300	500
Pressure in mm. Hg..	1×10^{-5}	1.9×10^{-6}	1.7×10^{-7}	1.2×10^{-7}	2×10^{-7}	2.4×10^{-8}

While these results are only relative the importance of heat treatment is clearly shown.

The cleaning of the glass is very important in high vacuum production It was found that the removal of grease by potassium bichromate solution followed by a prolonged washing with boiling water to remove soluble salts proved most effective.

The electric oven in which the gauges and bulbs were placed was kept at a temperature of 500° C. while the system was pumped for two hours.

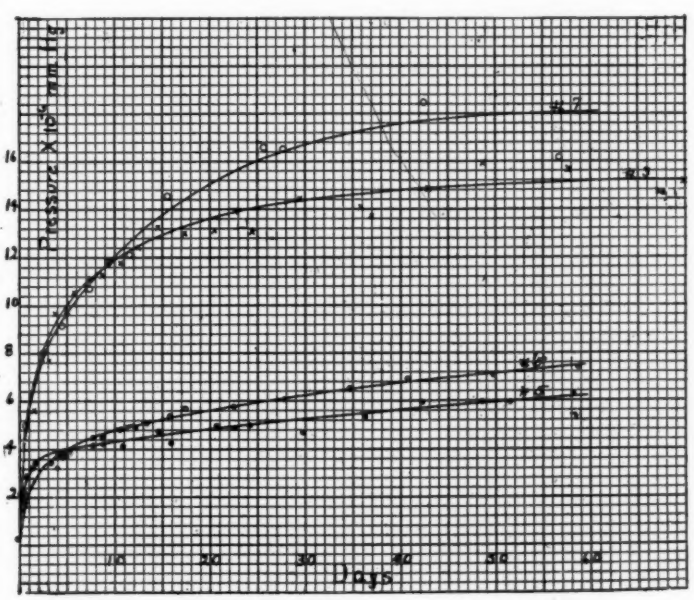

Fig. 1.

The glass would easily stand this temperature though it would collapse at 550° C. This margin of temperature was kept for safety. After the two hours heating and pumping the electric oven was removed and the bulbs and gauges were allowed to cool. After the pressure had been observed the sealing-off process was accomplished by heating the constriction with the pointed flame of a blowpipe. When the glass was near the melting point the gauge indicated a considerable increase in pressure.

The glass was kept heated near the melting point for about ten minutes while the pump continued to operate. The pressures before and immediately after sealing are given in the table below for four bulbs and gauges which had been given identical treatment.

	No. 3 (702-P).	No. 5 (702-E.J.).	No. 6 (702-P.).	No. 7 (702-E.J.).
Pressure before sealing off...	2.7×10^{-7}	3×10^{-7}	8.5×10^{-6}	9.7×10^{-6}
Pressure after sealing off....	1.1×10^{-6}	1.5×10^{-7}	3.4×10^{-7}	8.6×10^{-7}

These bulbs and gauges were securely mounted and the changes in pressure with time were observed. These results are shown in Fig. 1. It is noted that in all cases there is a rapid initial rise of pressure with time followed by a slower and more uniform change. No conclusions can be drawn from these data on the different grades of glass as to its suitability for vacuum work. Bulbs 3 and 6 were of Corning glass 702-P. while 5 and 7 were of 702–E.J. or Pyrex. It is observed that 5

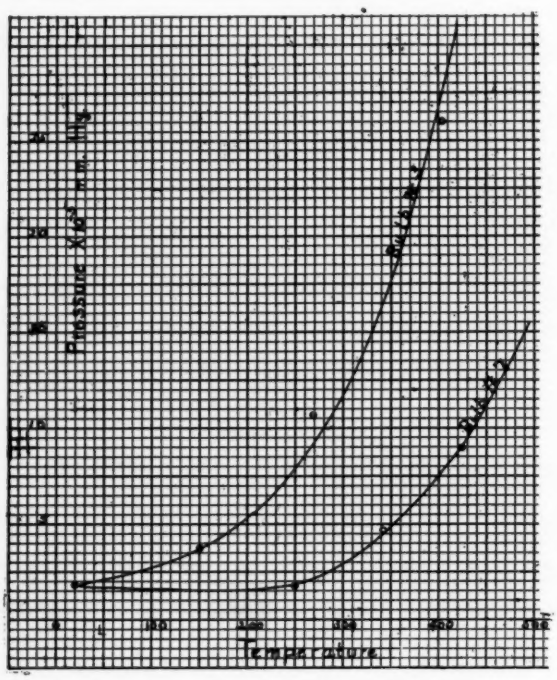

Fig. 2.

and 6 and 3 and 7 almost duplicate each other. It is also observed that bulbs 6 and 7 were pumped to the highest degree of exhaustion yet the pressure in no. 7 is the highest of all after a few days. It is noticed, however, that 5 and 6, which had the lowest pressure after sealing off, still have the lowest pressure after sixty days.

To determine the effect of subsequent heating, two of the bulbs and gauges were replaced in the oven and heated for one hour at increasing successive temperatures and the increased pressure resulting from each heating was determined. These results for bulbs 3 and 7 are shown in Fig. 2. It is seen that heating 7 to 250° did not change the pressure while for 3 the pressure increased with all increases of temperature. The changes of pressure at the lower temperatures have always been observed to be less rapid than at the higher temperatures.

This investigation shows that the vacuum in sealed vessels deteriorates with time, rapidly at first and then more slowly, and that subsequent heating even at temperatures lower than the heat-treating temperature results in increase of pressure due to further liberation of gases and vapors from the glass. No connection between different samples of the same glass or different glass can be established. It is quite probable that there are variations in the properties of different samples of the same glass quite as great as the variations between different glasses of about the same grade, for example, Corning 702-P and Pyrex.

THE JOULE-THOMPSON EFFECT FOR AIR AT MODERATE TEMPERATURES AND PRESSURES.

BY L. G. HOXTON.

SYNOPSIS.—In the experiments as described air was pumped first through a set of tubes designed to remove carbon dioxide and moisture, then through the throttling device or "porous plug" and finally back to the pump. The plug and tubing immediately leading to it were immersed in an oil bath thermostat. The bath temperatures, for the most part, lay between 0° and 100° C., the mean pressures, from 4.5 to 6.4 meters of mercury, while the pressure-drop varied between 0.25 and 0.80 meters of mercury. The temperature-drop was measured by platinum resistance thermometers differentially connected. The plug was of the radial flow type originated by Regnault, roughly cylindrical in form, through the walls of which the air flowed toward the axis, escaping finally through one end. The accidental errors were apparently of an order under one per cent.

The Joule-Thomson coefficient (μ) was found to have a decreasing linear variation with increasing mean pressures. Its dependence upon both temperature and pressure are embodied in either of two empirical formulas, namely:

$$\mu = +0.3935 - 0.00691p - 0.001835t + 0.00000134t^2 + 0.0000325pt$$

$$\mu = -0.2599 + 182.0\frac{1}{\tau} - 552.4\frac{p}{\tau^2},$$

all pressures being measures in meters of mercury, t in degrees C., while $\tau = 273 + t$.

These formulas are applied to calculate the temperature of the ice point on the thermodynamic scale, to reduce to the same scale the readings of the constant pressure air thermometer and to discuss the variations of c_p with pressure. Good agreement with the results of other work is found in the second and third cases, while in the first, the result, in common with that found from other Joule-Thomson data, is higher than the result found from the characteristic gas equations.

The paper includes a brief historical summary of previous experimental work, a discussion of several theoretical points and of sources of error, especially heat leakage.

CONTENTS.

Introduction.
Historical Outline.
General Conditions of Present Experiments.
Description of Apparatus.
Early Experiments with Axial-flow Plugs.
Preliminary Experiments with Radial-flow Plugs.
Final Results and Conclusions.
Acknowledgments.
Bibliography.

INTRODUCTION.

A NEED for new determinations of the Joule-Thomson effect has long been recognized by students of thermodynamics, and it has found expression occasionally in the literature touching this subject.

Such data, as is well known, still preserve their original importance for the study of molecular attractions in gases and for the establishment of the thermodynamic scale of temperatures. More recently they have acquired interest for the engineer, namely for the computation of steam tables, ammonia tables and the like. The latter aspect has been discussed by Davis.[1]

Aside from the desirability of experimenting over a wide range, increased accuracy is obviously one of the first improvements in the data that is needed. The published results have been considered too uncertain on the whole, and in many cases too difficult of interpretation to be of great value. The present paper is devoted largely to the latter phase of the problem and is therefore somewhat limited in scope.

At first it was planned to work with several gases and cover a considerable extent of temperatures and pressures. However, a year's experimentation at the Johns Hopkins University with carbon dioxide disclosed many difficulties in the way of obtaining results at all consistent with one another. It was decided, therefore, to confine the work for the time being to an attempt to develop a reliable method and to proceed to this end by ways that seemed the most direct. Side problems were to be avoided wherever possible. Hence the range of temperatures and pressures were restricted within the limitations of the resources already at hand. Air was chosen as the gas to be experimented upon, chiefly because of its availability and the small amount of attention to contamination and slow leaks in the apparatus that its use would entail. Results from pure gases are, of course, to be preferred in general, yet those obtained from air are not without interest as regards thermometry and for comparison with work on air in this and related fields.

It is hoped that in the experiments to be herein described, most of the larger sources of error have been overcome. The accidental errors are small for work of this kind, being of an order considerably under one per cent. Perhaps there is a systematic error outstanding, indicated possibly by the relatively large value computed for the thermodynamic temperature of melting ice. The sources of such error, if existent, have so far not been found. Further experiments with other gases should throw light upon this matter, especially those gases whose expansion coefficients have been determined with great care by Chappuis, namely, nitrogen, hydrogen and carbon dioxide. The author would welcome, in the meantime, any suggestions occurring to the minds of those interested in this subject.

Historical Outline.—Although a historical summary of experimental work down to 1905 has been given by Kester, in a paper to be taken up

later, a complete outline would seem desirable here, first to supply a few omissions and secondly to include a considerable amount of new material.

After the original classical experiments of Joule and Thomson,[2] carried out in the years 1852 to 1862 on air, nitrogen, oxygen, carbon dioxide and hydrogen, whose work is too well known to need further comment, one of the early experimenters to enter this field was Regnault.[3] His work has often been overlooked. The most interesting feature of his apparatus is the ingenious design of its porous wall or throttling partition, which was not in the form of a "plug." It was a hollow enclosure through the wall of which the gas flowed from the outside to the interior. A hole in the wall was provided for the continuous escape of this gas. The obvious purpose of this design was to provide thermal protection. In this respect it seems greatly superior to the plug form used by Joule and Thomson. Yet Regnault abandoned the work as futile with an expression of regret at the waste of time spent on a research so "sterile." He found that the temperature readings within the enclosure were too uncertain to have any meaning. In the light of subsequent advances in methods of measurement, several possible causes for these troubles might be assigned, but, especially since his descriptions are not full in detail, their discussion here might not be profitable.

The forms of throttling device or "plug" introduced in these two investigations are typical. Most of the subsequent experimenters have employed the form used by Joule and Thomson, possibly because the work of Regnault, as far as it went, has had little attention directed to it. In 1910 Burnett and Roebuck,[4] in a paper entitled "On a Radial Flow Porous Plug and Calorimeter," proposed a plug on the Regnault principle adding improvements in detail. Their work, however, was entirely independent. Later Roebuck[5] used apparatus of this type on liquid water in order to determine the mechanical equivalent of heat. Only two other experimenters so far have published work with similar apparatus with gases, namely, Trueblood[6] and the present author. Following the usage of Trueblood the term "axial flow" will be applied to the plug form used by Joule and Thomson to distinguish it from the other or "radial flow" type.

One should not fail to note in this connection that certain protective features of the radial flow principle have come into use more or less generally in continuous flow calorimetry, as for example, in the work on C_p by Swann[7] and by Scheel and Heuse.[8]

Hirn[9] carried out throttling experiments upon steam, using an orifice. Work of others on steam, namely, Griessmann,[10] Grindley,[11] Peake[12]

and Dodge,[13] has been discussed by Davis.[14] As Davis states, the first named used a porous plug very much like that of Joule and Thomson, while the others used a throttling calorimeter, their work being undertaken for the "purpose of determining the variation of the specific heat of steam with pressure and temperature, an investigation which has since been more satisfactorily accomplished in other ways."

Cazin[15] in 1870 published an account of experiments which were essentially modifications of the Gay-Lussac free-expansion experiment. His apparatus was complicated, and, as he admits, his results were qualitative.

Natanson[16] in 1887 described porous plug experiments on carbon dioxide at 20° C. only. His pressure-drop was about one atmosphere and his highest absolute pressure 25 atm.; and between the lowest and highest pressures he found a decided dependence of the cooling effect upon pressure, whereas Joule and Thomson had not noted (up to 6 atm.) any such effect. This dependence does not agree with that found later by Kester and is in the opposite sense from that found for air in the present paper.

Mention is made here of work reported by Witkowski,[17] who carried out experiments on air at high pressures, passed through a succession of porous plugs. Only a brief abstract of his paper has been available, which contains no quantitative results. There is no obvious theoretical advantage to be gained by employing a succession of plugs. All the data could be had from a single plug by properly varying the pressures and bath temperatures.

Kester[18] in 1905 extended the work of Natanson on carbon dioxide to temperatures between 0° and 100° C. finding also a dependence upon pressure. The results of the two observers are not in agreement, Kester's results at the same temperature (20° C.) being independent of pressure up to the highest pressure employed at that temperature, namely, 41 atm., while the work of Natanson yielded a positive pressure coefficient. At one pressure, 26.4 atm., Kester found an indication of a positive coefficient.

Olszewski[19] performed experiments (using not a porous plug but a throttle valve) on hydrogen in order to determine its "inversion temperature" as bearing upon the problem of its liquefaction. The high pressure of the experiment varied from 117 to 170 atm. and the low pressure was uniformly one atmosphere. The one datum of this experiment was $-80.°5$ for the inversion temperature under these conditions. The effect observed was, of course, an integrated one and leaves much to be desired for application of thermodynamic equations.

Five years later[20] (1907) he did the same thing for nitrogen and air, finding a series of inversion points for magnitudes of the pressure-drop varying from 160 atm. to 30 atm.

Rudge[21] carried out (1909) a few experiments on carbon dioxide supplied on the market in the form of "sparklets" for making carbonated water. The duration of each experiment was but a few minutes and their author does not attach great importance to the results, but offers them in view of the scanty known data. It would seem that the ideal conditions for continuous-flow methods could hardly be realized in so short a time.

Bradley and Hale[22] in the same year carried out experiments upon "the nozzle expansion of air at high pressure," *i. e.*, from initial pressures of 70 to 200 atm. to final pressures of 1 atm. Their temperatures extended from 0° C. to − 120° C. approximately.

Their apparatus was a liquefier of the Hampson type and the air expanded through a specially constructed "nozzle." Their particular problem was the process of liquefaction; and their results were in qualitative agreement with those of Joule and Thomson. These experiments would seem subject to error from heat leakage.

Again in the same year (1909) Dalton[23] carried out at the Leyden laboratory similar nozzle experiments in air at 0° C. only and for pressure drops from about 5 to 40 atm. His results agree with the Joule and Thomson figures at 0° C., and he notices no pressure effect, although his curve would indicate an extremely slight negative coefficient.

Vogel,[24] whose original papers have been unavailable, carried out porous plug experiments in the Laboratory of Technical Physics of the Techniche Hochschule in Munich. He was looking for a pressure effect and found a negative coefficient. The temperature of his experiments was 10° C.

Noell,[25] whose original paper likewise has been unavailable but an abstract[26] of which is at hand, continued the work of Vogel in the same laboratory. His pressure-drops were 6 and 8 atmospheres while the arithmetic mean of the absolute high-side and low-side pressures varied from 25 to 150 atm. His high-side temperatures varied from − 55° C. to + 250° C. He worked with air only. He found a pressure as well as a temperature effect which he embodied in the interpolation formula:

$$\frac{\Delta T}{\Delta p} = \frac{50.1 + 0.0297\,p}{T} + \frac{14830 - 1.674\,p}{T^2} + \frac{366000 - 19093\,p}{T^3} - (0.122 + 0.0000157\,p).$$

This is evidently an empirical expansion in descending powers of T, whose coefficients are linear functions of p.

The pressure units seem to be kg. per cm.^{2} in the left-hand member and atmospheres on the right. The difference in any case would not be more than about 3 per cent., but the author does not make it clear. The deviations of his observed values from those calculated by this formula vary from 2 per cent. to 6 per cent. at the lower temperatures, to 50 per cent., and over at the highest temperatures. Nevertheless his work seems to be more systematic and satisfactory than that of his predecessors, certainly for air.

Cuts of the apparatus of Vogel and Noell may be found in Jellineks' Lehrb. d. Ph. Chem., Vol. I., 1914. They show two forms of plug, the earlier being of the axial flow type, the later, a combination of the axial and radial flow types in which an inner axial flow plug was surrounded by a jacket containing the inflowing high side air at bath temperature.

Buckingham[27] has proposed a modified form of the porous plug experiment in which the process is to be rendered isothermal by supplying heat, say electrically, to the plug in just the sufficient amount to prevent the temperature-drop. If there should be a heating effect, as with hydrogen, there would have to be devised some way of abstracting heat from the plug. No extended experiments by this method have been published.

Trueblood[6] carried out experiments at about the same time as those of the present author, which are described in a paper entitled "The Joule-Thomson Effect in Superheated Steam; I. Experimental Study of Heat Leakage." He limited the work to a single temperature and pressure and carried out a thorough and effective study of the heat leakage. Extensive tests, under varying conditions, were made upon a number of different plugs of the axial and radial flow types. He concluded the latter to be the superior and that it is capable of yielding reliable results. A remarkable form of indirect heat leak was found for the radial flow type, which he named the "regeneration effect." This matter will come up later under a separate head.

The experimental work in this field, thus briefly summarized, lends itself only in small measure to the application of thermodynamic equations owing to the difficulty or impossibility of attaching a definite meaning to a large part of it. Thus the only work found available for the calculation of the thermodynamic scale of temperatures hitherto published[28, 29, 30, 31] has been that of Joule and Thomson principally, with later computations including the results of Natanson, Kester and, in one instance, of Olszewski.

It has seemed to the author that in some cases the programs of experimentation have been, perhaps, too ambitious in the direction of extreme

temperatures and pressures with the result that an oversight of vital details affecting accuracy was quite possible. The intention to limit the present work in the way mentioned at the beginning was confirmed by considerations of this sort.

General Conditions of Present Experiment.—The range of temperatures was confined approximately to the fundamental interval—actually from 15° C. to 90° C., although experiments had been started at 110° C. when the apparatus called for repair. The term "pressure" in the title of this paper refers to the arithmetic mean of the absolute pressures on the two sides of the plug. The range lay from about 6 to 8½ atmospheres, or more precisely, from 4.5 to 6.4 meters of mercury. The pressure-drop ranged from 0.25 to 0.80 meter of mercury. Pressures throughout this paper will be expressed in meters of mercury. For the immediate purpose of these experiments outlined above, the obvious gas to be chosen was, of course, air.

REMARKS ON THEORY.

The general theory of the plug experiment has been given so often in treatises and in journal articles that a full treatment of it here would be out of place. As much, however, should be given as is sufficient to define the necessary symbols and to develop such special formulæ as are needed in the computation of results.

The function $u + pv$, the "total heat" or so-called "*enthalpy*" of Kamerlingh Onnes, is supposed to be the same in the regions of equilibrium above and below the plug. Let us call it H. Then the Joule-Thomson coefficient (μ) is defined as the limiting value of the ratio of the temperature-drop to the pressure-drop, when these each approach zero, under the condition $H = const.$, that is,

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \quad (1)$$

Graphically represented this is the slope of the tangent to the curve $H = const.$ on the (p, T) diagram. From (1), through the application of the second law of thermodynamics, follows the general relation always associated with the porous plug experiment, namely,

[1] It may be worth while to note, in passing, that inasmuch as one often finds confusion of statement between the free expansion or Gay-Lussac effect and the Joule-Thomson effect, the distinction between the two may be brought out by expressing the two as

$$\left(\frac{\partial T}{\partial p}\right)_u \quad \text{and} \quad \left(\frac{\partial T}{\partial p}\right)_H$$

respectively.

$$T\left(\frac{\partial v}{\partial T}\right)_p = v + \mu c_p.^1 \qquad (2)$$

It will be shown later that μ was found experimentally to be a function of temperature and pressure. In the search for an empirical formula to express this relation and one which would have a little more rational basis than a mere power series, resort was had to the equation of van der Waals. While this equation does not strictly fit the measurements on isotherms, yet the author is in accord with Berthelot[32] in thinking of it as a valuable index to broad features of the properties of gases and as being something more than an empirical interpolation formula.

Applying to van der Waals' equation, namely

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

the relation (2) above, we get, keeping only terms of the *second order* in the small quantities a and b, the relation

$$\mu c_p = -b + \frac{2a}{RT} - \left(\frac{6ab}{R^2T^2} - \frac{4a^2}{R^3T^3}\right)p. \qquad (3)^2$$

[1] Thus calling s the entropy

$$Tds = du + pdv = dH - vdp,$$

or, putting T = constant,

$$T\left(\frac{\partial s}{\partial p}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T - v.$$

But

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \text{ ("thermodynamic relation")}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H = -c_p\mu.$$

$$\therefore \quad T\left(\frac{\partial v}{\partial T}\right)_p = v + \mu c_p. \qquad (2)$$

A short proof quite similar to this has been given by Callendar.[29]

[2] Expanding van der Waals's equation,

$$pv + \frac{a}{v} - bp - \frac{ab}{v^2} = RT,$$

and applying the operator $(\partial/\partial T)_p$ to both sides,

$$\left[p - \frac{a}{v^2} + \frac{2ab}{v^3}\right]\left(\frac{\partial v}{\partial T}\right)_p = R.$$

$$\therefore \mu c_p = T\left(\frac{\partial v}{\partial T}\right)_p - v = RT\left[p - \frac{a}{v^2} + \frac{2ab}{v^3}\right]^{-1} - v$$

$$= \left[RT - pv + \frac{a}{v} - \frac{2ab}{v^2}\right]\left[p - \frac{a}{v^2} + \frac{2ab}{v^3}\right]^{-1}$$

$$= \left[-b + \frac{2a}{pv} - \frac{3ab}{pv^2}\right]\left[1 - \frac{a}{pv^2} + \frac{2ab}{pv^3}\right]^{-1},$$

on substituting the value of $RT - pv$ from the expanded equation of van der Walas and

Now the variation in c_p within the limits of the present investigation is small or at most may be considered a linear function of p. If then we neglect the term in T^3, μ should be a function of the form

$$\mu = A + \frac{B}{\tau} + p\frac{C}{\tau^2}, \tag{4}$$

where $\tau = 273 + t$.

The first two terms are those of the complete formula of Rose-Innes.[30] It will be noted that the pressure effect is linear and even then only comes in if we retain second order terms. Later this formula as well as a five-constant power series linear in p and of the second degree in $t°$ C. will be fitted to the observations. Obviously the second power of τ in (4) could be replaced by the first power and the adjustment be empirically just about as good within the small range of observed temperatures, but the second power is retained to keep closer to the original basis.

DESCRIPTION OF APPARATUS.

The Air Circuit.—The air-circuit and the disposition of the various parts are shown in Fig. 1. Air is drawn in by the compressor at the intake A which is kept open all the time in order to replenish the supply of air lost by slow leakage. The air then passes upward through the driers D and D', the former containing a column of about a meter of calcium chloride, the latter about half a meter of soda-lime to remove carbon dioxide, followed by a half meter of calcium chloride to remove the water put in by the reaction of the carbon dioxide with the soda-lime. Water trapped in the lower end of D from the air under compression is

factoring out p. Let us now expand the right hand bracket and in all expressions retain no order in a and b higher than the second. Then

$$\mu c_p = \left[-b + \frac{2a}{pv} - \frac{3ab}{pv^2} \right]\left[1 + \frac{a}{pv^2} - \frac{2ab}{v^3} + \cdots \right]$$

$$= -b + \frac{2a}{pv} - \frac{4ab}{pv^2} + \frac{2a^2}{p^2v^3} + \cdots.$$

Now, in the second order terms, pv may be replaced by RT alone. In the first order term we must put $pv = RT - a/v + bp$.

$$\therefore \frac{2a}{pv} = \frac{2a}{RT}\left[1 - \frac{a}{vRT} + \frac{b}{RT}p \right]^{-1}$$

$$= \frac{2a}{RT} + \frac{2a^2}{vR^2T^2} - \frac{2ab}{R^2T^2}p + \cdots$$

$$= \frac{2a}{RT} + \frac{2a^2}{R^3T^3}p - \frac{2ab}{R^2T^2}p + \cdots$$

$$\therefore \mu c_p = -b + \frac{2a}{RT} - \frac{6ab}{R^2T^2}p + \frac{4a^2}{R^3T^3}p \cdots$$

Q. E. D.

drawn off by the valve B. This was done usually once during a run which lasted some four or five hours.

From the driers the air is carried through a quarter-inch gas pipe to the plug apparatus proper in a neighboring room. Here it passes first through a series of throttling needle-valves t, then through a third drying tube D'' containing phosphorus pentoxide. From this it passes

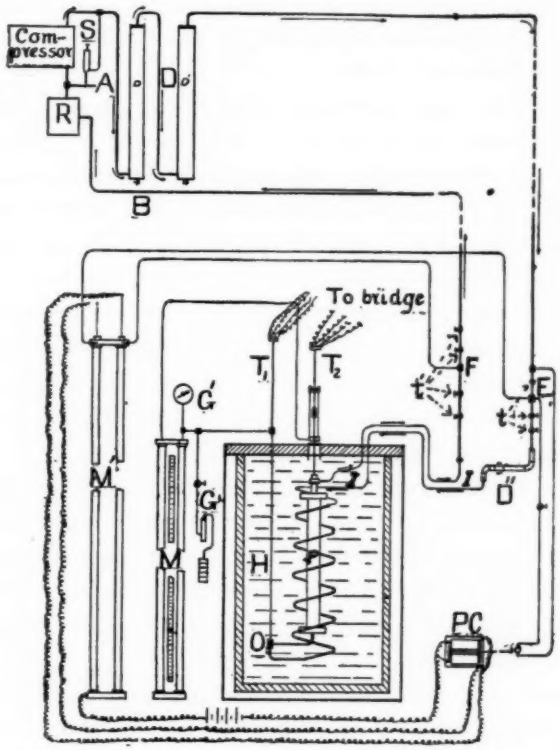

Fig. 1.

through copper "automobile tubing" of about 5 mm. outside diameter, into the bath, under the surface of which the automobile tubing continues for about two meters, connecting thence with a coil of larger pipe of brass and about one cm. internal diameter and 6 meters in length. This coil terminates in the plug casing P. After passing through the porous plug, the air leaves the casing by way of another length of automobile tubing much shorter than the first and soldered parallel with it for a purpose stated below.

Interchanger.—For a length I, I of about a meter the tubes are soldered together side by side, forming thus a heat interchanger, so that when the bath and the room were at considerably differing temperatures the

air leaving the bath would be brought to approximately room temperature and the air entering the bath would be brought to approximately the bath temperature in advance. This device was found to be necessary for two reasons: first, it conserved the heat of the bath and improved its temperature regulation, and secondly, it prevented the throttles t' in the return line from progressively warming, a condition which was found seriously to interfere with pressure regulation. This warming of the valves would gradually change their opening and hence change the rate of flow of air through them.

After leaving the low pressure throttles t' the air returns to the compressor by way of a receiver R of about 10 liters capacity. Curiously enough, this receiver, when placed on the low-pressure side, was quite effective in reducing the pulsations in the air-circuit produced by the intermittent action of the compressor while no receiver was needed at all on the high pressure side.

Pressure Regulation.—It is obviously necessary to provide means to keep constant the pressures at all points, and especially the pressure-drop in passing through the plug. The heat of compression liberated here might quite mask the Joule-Thomson effect. It was observed, for instance, on one occasion, that a fluctuation in the pressure-drop of 0.1 per cent. resulted in a fluctuation of about 5 per cent. in the temperature-drop and consequently by 5 per cent. in the observed Joule-Thomson effect. Special precautions therefore were necessary to provide good pressure regulation. Further, this had to be automatic on account of the necessity for the observer to work alone. Fluctuations of 20 per cent. in the power service had to be cared for.

Rough pressure regulation was attained as a preliminary by placing an adjustable spring safety-valve S (Fig. 1) in a by-pass from the high pressure to the low pressure lines near the compressor. This was usually set so that the difference on the two sides of the valve would be from 80 to 160 lbs., gauge reading, depending upon the pressure drop at the plug.

Superposed upon this was a finer method of regulation which was designed to control the pressure drop between the points E and F. This was carried out by means of an electrically controlled valve mechanism actuated through contacts in a mercury manometer M', which was connected in at the points E and F. The valve mechanism is indicated at PC which is connected as a by-pass to the first or upper throttle t so that when opened the flow of gas is increased.

The two electrical contact-points of the manometer M' are set at any desired difference of level such that the tops of the mercury columns play just under them when the device is functioning properly. If for

some reason the pressure difference decreases, the lower contact will be made, and this will actuate one of the electromagnets at *PC*, which, through setting in motion a train of gears will open the by-pass needle-valve at *PC* very slowly, thus supplying an increased flow of air and bringing the pressure difference back to its proper value. A similar action in the reverse direction will take place if the pressure drop exceeds the limits set by the positions of the contact points. When the pressure is at its proper value, the valve at *PC* is at rest.

There were, of course, small fluctuations in pressure remaining, even though this device gave much finer regulation than did the safety-valve *S*. These residual fluctuations were practically damped out by the throttles *t* and *t'* lying between the points *EF* and the plug. The greatest variations in the pressure drop at the plug were of the order of 0.1 mm. of mercury and usually too small to be observed.

The throttles *t* and *t'* together with the safety-valve *S* served, in addition, as a means of setting the absolute pressures in the system to any desired values.

Mounting of Thermometers.—T_1 and T_2 (Fig. 1) are brass tubes housing the stems of platinum resistance thermometers, one of which is situated in the elbow *O*, on the high-pressure side of the plug, and the second in the interior of the plug casing *P*. Emerging from the tops of these tubes and passing through sealed joints in appropriate hard rubber insulation are the leads which connect through heavy lamp-cords to the bridge. Into the latter they are connected differentially as will be described later. Thermometer tube T_2 has a telescoping joint indicated in the diagram whose purpose is to permit one to shift vertically the thermometer and so to explore the region on the low-pressure side of the plug in order to study the distribution of temperature therein.

The Differential Manometer.—From the sides of the stems of the thermometers T_1 and T_2 lead two small tubes connected to the manometer *M* as shown in Fig. 1. The latter is thus put in communication with the spaces occupied by the thermometer coils themselves and is intended to measure the pressure-drop between the high and low pressure sides of the plug. The manometer was somewhat over a meter in height and was furnished with a brass meter-bar of the "H" form made by the Société Genèvoise. This was placed between the tubes and read by a micrometer telescope from a distance of about one meter, the tube and scale being in the same field of view at one time. The crosshair was leveled by setting on the image of the level surface of mercury placed in a glass cell with plane sides at the same distance from the telescope as the manometer. The heights of meniscus were read off in order to

supply data for the capillary correction which never exceeded 1 mm., and if omitted, would not have introduced an error exceeding 1/500 of the observed pressure drop, and even that would be within the accuracy demanded, for errors somewhat less than one per cent. in the Joule-Thomson effect came in from other sources. The corrections, however, were applied making use of the tables given in Kohlrausch, "Physical Measurements," 3d edition (English), p. 440. The internal diameters of the tubes varied from 5.0 mm. to 5.7 mm. along the portions where readings were made.

The readings were likewise reduced to 0° C., making use of tables given in Landolt and Börnstein's "Tabellen," 3d Aufl., pp. 34 and 35. Pressures throughout this paper are expressed in meters of mercury at 0° C. at the University of Virginia. The value for g (980 cm./sec^2) is needed only in final computations.

Pressure Gauges.—To the high-pressure side of the differential manometer were connected a piston gauge and a dial gauge, G and G' (Fig. 1) respectively. The latter was used for setting to the desired absolute pressures; while the former yielded their correct measure. The piston was of 3/8" drill rod mounted in a snugly fitting brass cylinder provided with a leather packing at the top, so curved as to become tighter as the pressure increased. This also insured that the effective area of the piston was its own cross section and not a compromise between this and that of the bore of the cylinder. Provision was made for rotating the piston, in a manner similar to that carried out by Amagat, in order to eliminate the static friction.

The diameter of the piston measured by two micrometer calipers came to 0.9536 cm. giving an area of 0.7142 sq. cm. Thus 1 kg. on the piston corresponded to a pressure of 1.030 meters of mercury at 0° C. and at the same locality.

The weights were adjusted by a set of platinum plated weights furnished by Rüprecht of Vienna, and brought to within 0.02 per cent. of accuracy or about one fiftieth of the errors of reading of the gauge when in use. Great accuracy was not needed, for it will be seen that the effect of pressure on the Joule-Thomson coefficient is small.

Bath and Thermostat.—The bath was about 90 cm. deep and 30 cm. in diameter with triple walls of sheet brass. The space between the middle and inner walls was filled with asbestos, and that between the middle and outer was designed for the circulation of steam, but not so used. The outer wall was lagged with asbestos. The cover was lagged with about 10 cm. thickness of cotton waste which has been all that was necessary for temperatures up to 130° C. "Renown engine oil" made

by the Standard Oil Co. was used to fill the bath and, on account of its great thermal expansion, a siphon overflow had to be provided. Rapid circulation was provided by two motor-driven propellers on one vertical shaft rotating in a well. The stirrer and heating coils are not shown in the diagram.

Heating was applied electrically from a 220-volt D.C. circuit, through four coils totaling a capacity of one kilowatt. These could be cut in independently in series or in parallel, various combinations being used, including auxiliary resistances, according to the temperature of the bath.

Thermostatic control was obtained by keeping a steady current in some of the resistances and varying the current in the remainder. This was done automatically by the wheatstone bridge type of thermostat similar in principle to that described by Darwin[33] and by Randall[34] and later made use of by the Leeds and Northrup Co. Its performance was quite good, keeping the bath, under the best working conditions,

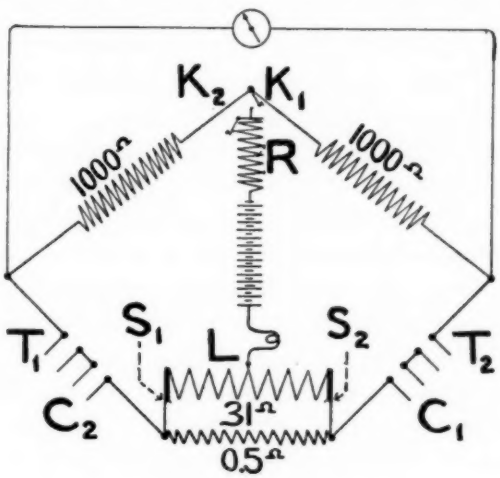

Fig. 2.

constant to 0°.001 C.; and in but few instances was the fluctuation more than 0°.004 C. It is a remarkably convenient form of apparatus for setting at any desired temperature.

The use of a 220-volt D.C. supply is perhaps open to criticism; but with care in insulation, trouble from leakage through the galvanometers from this source was avoided. It was, moreover, the only kind of power-supply at hand.

The Wheatstone Bridge.—Resistance measurements were made in terms of a decade resistance box manufactured by the Leeds and Northrup Co. of Philadelphia. The coils needed (from 30 ohms down) were cali-

brated twice, two years apart, and found to remain constant to well within the required accuracy.

The thermometers on the high and low-pressure sides of the plug were connected into the bridge differentially as shown in Fig. 2, where T_1 and T_2 represent the wires leading to the thermometer coils and C_1 and C_2 the compensation leads which will be described below.

The quantity desired is the difference in the effective resistances of the two thermometers. The Carey-Foster[35] method was employed because it measures directly the difference between resistances and eliminates all fixed contact- and lead-resistances. The mercury commutator for effecting the transposal of the resistances to be compared, which in this case are $T_1 + C_2$ and $T_2 + C_1$ is omitted from the diagram.

It will be noted that the arrangement of battery and galvanometer is not that usually published in the text-books. By putting, as indicated, the battery instead of the galvanometer in series with the sliding contact and by having no key in series with the galvanometer the error of thermal E.M.F.'s was eliminated. This arrangement follows the practice of the Bureau of Standards. It has worked admirably and obviated the necessity of reversing the battery current.

The slide wire S_1LS_2 was a "Students' Potentiometer" manufactured by W. G. Pye & Co., of Cambridge, England, and consists of a wire wound in a helix on a slate drum and with sliding contacts S_1S_2 at the ends. It has 10,000 divisions from end to end and a resistance of 31 ohms approximately. This being too high for direct use, it was shunted by a resistance of about half an ohm made of manganin wire. With this arrangement and by repeated tests at different dates the value of one division was determined to be 0.00005666 ohms or, in terms of the particular thermometers used, equivalent to about 0.0005° C. The precise conversion of bridge readings into degrees will be given later.

The errors due to the variability of the sliding contact resistances S_1 and S_2, being connected in series with a resistance as high as 31 ohms, proved to be negligible. For, by test, the uncertainty was not over 0.12 division (0.00006° C.) while, in the final readings, only the nearest whole division was taken into account. All other junctions in the four arms were either amalgamated or soldered. The wire S_1LS_2 was calibrated several times and was found uniform to a small fraction of a division.

For resistance thermometry, and with the battery connected between the thermometers as shown, the more sensitive arrangement is to have high-resistance ratio-arms; hence a high value for these, namely, 1,000 ohms, was employed.

The key K_1 opened and closed the battery circuit while K_2 in conjunction with the resistance R, permitted the observer to vary the battery current for the purpose of obtaining corrections due to the heating effect of the measuring current in each thermometer.

The Platinum Resistance Thermometers.—These were of the four-lead compensated type introduced by Callendar.[36] The ends of the compensating leads were united by a short length, about 1 cm., of the same sort of wire as that used for the thermometer coils. The thermometers were connected differentially into the bridge, thermometer No. 1 and compensating-lead No. 2, being connected in series on one side, while thermometer No. 2 and compensating-lead No. 1 were in series on the other side. These connections (Fig. 2) are lettered T_1, C_2 on the left, T_2 and C_1 on the right. In differential connections, the need for the compensation leads is very much reduced, but, in the present instance, they were kept in to be on the safe side, especially in view of the fact that the depth of immersion of the two thermometers was not quite the same.

The wire for these thermometers was obtained from the Cambridge Scientific Instrument Co., Ltd., very pure and recommended by them for thermometer work, in which they make a specialty. The diameter of the wire was about 0.03 mm., and its length such as to give a change in resistance of about 11 ohms for a change in temperature from 0° C. to 100° C. It was wound upon the usual crossed mica frames in the form of a compact cube approximately 5 mm. each way. The fineness of the wire and the compactness of its mounting was for the purpose of allowing exploration of the space on the low-pressure side of the plug.

The four leads were sealed into the ends of a glass tube as appears at T_1 or T_2, Fig. 3, and passed thence up the tube and out through a wax-sealed joint into the room whence they were connected to the bridge by heavy No. 14 lamp-cord about 3 meters long each.

The thermometer coils were exposed to the flowing air in some of the preliminary experiments, but later, copper foil caps indicated by the dotted lines at T_1 and T_2 were slipped on. This made the galvanometer considerably steadier and did not introduce an objectionable lag because the copper caps should take the temperature of the gas before the walls of the enclosure.

The glass tubes containing the leads, after emerging from the air channels, were enclosed in larger brass tubes of $\frac{1}{8}''$ pipe size (the brass tube for T_1 shown in the diagram is larger than natural size), which came in contact with the bath and allowed air-connection to the differential manometer. The immersion of T_1 was about 44 cm. and that of T_2

about 34 cm. under the bath. The latter immersion was extended by a lagged air-space above the bath's surface by about 12 cm. This was thought sufficient to eliminate the effect of heat conduction along the leads inside the glass tubes in spite of the stagnant air-space by which the leads were surrounded.

The electrical insulation proved sufficient at all times. Repeated tests were made; in fact, the bridge wiring was arranged so that the thermometer insulations between pairs of leads could be coupled in parallel and the combination thrown in series with the galvanometer and a battery of 30 volts. This test, as a matter of precaution, was made a part of the routine of observation. In dry weather the galvanometer was not sensibly deflected, while in one or two instances in damp weather a film seemed to form on the outside insulation whose resistance was of the order 20 megohms. This obviously would not affect the measurements.

Several tests were made for a possible effect of pressure on the resistance of the thermometers but none was found.

Application of Callendar's Formulæ.—These were adapted to the work in hand, as embodied in equation (8) below, in the following manner, beginning with the formulæ themselves, namely:

$$t_p = 100\frac{R - R_0}{R_{100} - R_0} \text{ (defining the "platinum scale")} \qquad (5)$$

and

$$t - t_p = \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} \text{ (correcting to the hydrogen scale),} \qquad (6)$$

where δ is a quantity to be determined by experiment for the sample of platinum wire used.

Now, if Δt is a small temperature change, we get from (6)

$$\Delta t = \Delta t_p\left\{1 - \frac{2\delta}{10000}(t - 50)\right\}^{-1}$$

$$= \Delta t_p\{1 + 0.0003(t - 50)\} \qquad (7)$$

to the first order of approximation, if we put $\delta = 1.50$. This value, given by the Cambridge Scientific Company, who furnished the wire, was accepted as sufficiently accurate. For it is evident that its omission altogether could not alter the right hand member of (7) by more than 1.5 per cent. in the range from 0° to 100° C. covered in these experiments.

If μ_{tp} therefore, is the value of the Joule-Thomson coefficient observed in terms of the platinum scale and μ in terms of the hydrogen scale, then we have

$$\mu = \mu_{tp}\{1 + 0.0003(t - 50)\}, \qquad (8)$$

where μ_{tp} is the observed Joule-Thomson coefficient in terms of platinum degrees, and μ this coefficient calculated in terms of the gas-scale. (The distinction between the hydrogen and nitrogen scales need not be drawn for these measurements.)

The values of the fundamental intervals, i. e., $R_{100} - R_0$:

	Thermometer T_1	Thermometer T_2
May 12, 1915.....	10.952 ohms.	10.930 ohms.
" 14, "	10.963 "	10.932 "

Accurate knowledge of the fundamental interval of thermometer T_2 is all that is necessary, a matter that will come up later. The weighted mean for T_2 is 10.932 ohms.

The above tests were made with currents of air flowing past the coil at two speeds and likewise with the air stagnant. No variation of consequence occurred. The thermometers, moreover, showed themselves more than sufficiently stable during tests covering a year previous. The actual data then obtained cannot be used, however, on account of subsequent slight alteration in the thermometers.

Correction for Heating Due to Current.—The bridge current, of course, heats to some extent the thermometer coils themselves and this must be allowed for. Since the liberation of heat is proportional to the square of the current, the resulting small rise in temperature should follow the same law. Callendar's method is to double the bridge current and subtract one third the difference of the two corresponding settings from the first setting. The author found it a little more convenient to increase the bridge current in the ratio $1 : \sqrt{2}$. Thus the correction is immediately the difference in the two bridge settings.

Moreover, in order to make certain that this rule held under the present conditions a direct test was made with bridge currents in the ratio 1 : 2 : 2.5 : 4. The linear relation between the bridge readings and the square of the current was satisfactory. This held also in varying currents of air. Thus, where the rates of flow were 0, 2.9, 19, 36, 80, 132 and 250 cc./sec. the corrected bridge readings were 0.°016, 0.°018, 0.°015, 0.°015, 0.°015, 0.°015, 0.°014 respectively (reckoning from an arbitrary zero).

The order of magnitude of the heating correction in the final runs was 0.°01 C. The lower value of the battery current was 6 milliamperes.

Incidentally, the above data show that the length of the coil of pipe in the bath was sufficient to give the gas the temperature of the bath before it reached the plug.

Conversion of Bridge Readings to Degrees.—After the heating correction has been applied, the differential reading may be converted into degrees by a multiplying factor which was obtained as follows:

The unit for reading off settings was taken as one revolution of the slide wire drum and is called the "bridge unit" hereafter. Repeated standardizations of the wire at four different dates in terms of the calibrated ohm gave the value 0.005666 ohms per bridge unit.

Combining this with the figure just given of 10.932 ohms per 100° C. we get the factor 0.05178 degrees per bridge unit.

The values for μ obtained from the observations in terms of bridge units per meter of mercury are convertible into their proper values in terms of degrees per meter of mercury by the application of first this factor and then formula (8).

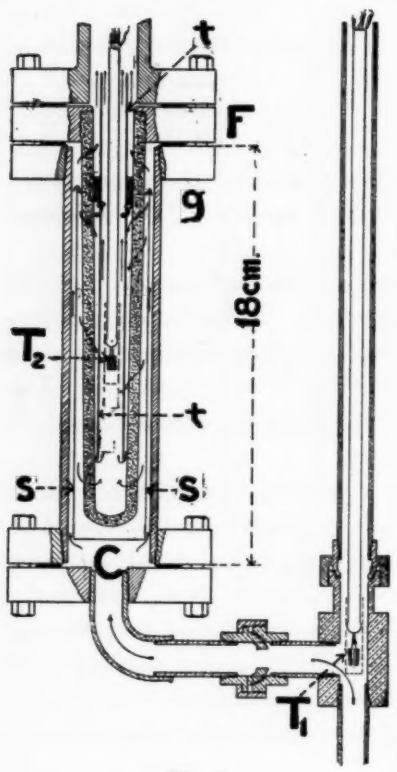

Fig. 3.

The Porous Plug.—The form of plug finally adopted was suggested by the research of Regnault already alluded to. Its longitudinal section is shown in Fig. 3 (dotted shading) the material being earthenware—a Pasteur filter. As may be seen, the flow of gas through the plug is radial toward an axis, and after passing through the plug wall its outflow takes place parallel to the axis. The purpose of this construction, as already pointed out, is to furnish thermal protection.

The whole apparatus shown in Fig. 3 is immersed in the bath, whose surface is 44 cm. above the point T_1. Air after traversing about 8 meters of pipe, in the bath, passes T_1, enters the plug casing at C and travels upward between the wall of the casing and a bright tinned radiation shield *ss*, as is indicated by the arrows. After passing over the top of the radiation shield it fills the space immediately outside the wall of the plug, through which it flows in two streams, divided by the "guard ring" *gg*. Within the plug is a glass tube *tt* which constrains the lower of these two streams to pass, all of it, past the thermometer T_2 while the upper stream is kept from passing the thermometer. Both streams pass out finally at the top.

The purpose of the guard ring is to avoid errors arising from conduction of heat along the material of the plug from its mounting F and ultimately reaching the thermometer inside.

The temperature of the plug in general is different from that of the casing. Radiation between the two would introduce an error. The radiation shield is to prevent this. As will be seen later, the radiation shield proved to be unnecessary but it was retained as a precaution, and is free from objection.

The construction of the plug casing (Fig. 3) permits the use of the principle of interchangeable parts. It may be seen that different plugs may be bolted in and that different sizes of casing as well may be employed. This proved a valuable feature in the preliminary experiments.

Preliminary Experiments.

Early Experiments with the Axial Flow Plug.—A number of experiments were carried out at the Johns Hopkins University in 1905–6, on carbon dioxide with a straight-flow plug of the type used in the Joule-Thomson experiments. Platinum resistance thermometers were used and so arranged as to be movable. The pressure-drops were of the order of one atmosphere. Plugs of various materials were tried, eider down, cotton, silk and paper. A vacuum-jacket was attempted and, what seemed better, the guard ring principle contained in a suggestion by Buckingham[27] was carried out. The porous plug was coaxial with a second annular plug designed to eliminate lateral temperature gradients.

The last arrangement improved things somewhat, giving one result in agreement with those of Joule and Thomson, but the general characteristic of the experiments was their lack of reproducibility.

On displacing the low-side thermometer, for instance, a steep temperature gradient along the axis was observed. The observed cooling effect continually fell off as the thermometer was further withdrawn. A shift, for instance, from 1 to 4 and 6 cm. distances cut the effect to about one half and one third respectively.

With varying rates of flow also the effect varied, but with a tendency toward a limit for the higher speeds. Natanson observed a variation with flow also. Perhaps we can thus account for the partiality of observers for high flows and plenty of gas. This feature and the ample dimensions of the apparatus of Joule and Thomson undoubtedly contributed to the accuracy of their results.

In addition, an enormous amount of time had to be consumed before a steady state could be attained, amounting to an hour and a half before a reading could be taken. Apart from other considerations, this would lead to a large chance for error unless the pressure regulation were watched very closely. A damped oscillation in the cooling-effect similar to that in the Joule-Thomson experiments was also observed.

It was decided, then, as already mentioned, to narrow the field and to concentrate on developing a method for the attainment of reliable results. What was to be desired was thermal protection, fine pressure regulation, and good temperature control. These problems have been taken up in the manner already described. The later experiments have been carried out in the Rouss Physical Laboratory of the University of Virginia.

Preliminary Experiments with Radial Flow Plug—Exploration.—Referring to Fig. 3, it will be remembered that the thermometer T_2 was capable of being shifted throughout the entire length of the plug. In the initial explorations the inner tube *tt* had not been introduced. The temperature distribution was fairly uniform except above the middle, and the correction for the heating of the thermometers due to the bridge current was much larger at the bottom of the plug, where the air-flow was slow, than at the top where the air-flow was faster. This led to the introduction of the tube and guard ring with the result that it not only reduced this heating correction but rendered the temperature distribution along the tube uniform to the order of 0.°001 C. Closer tests than this were not pressing nor possible, for time-fluctuations due to bath and pressure fluctuations were of this order of magnitude.

The final arrangement of the plug with tube and guard ring is almost identical with the arrangement published by Burnett and Roebuck (*loc. cit.*).

Rate of Flow.—This was separately measured by collecting the air over a pneumatic trough. Roughly the linear speed was found to be directly proportional to the pressure drop and independent of the absolute pressures, and hence of density. The result can therefore be simply expressed by a single number, namely 2.3 cm. per sec. per cm. drop of mercury. In the final runs this would mean a maximum speed within the tube *tt* of 180 cm. per sec., a little more than this at the bottom of *tt* (Fig. 3) and about double this around the thermometer caps. In the coil leading into the plug-housing, the speed was about the same.

Velocity Cooling.—The upper limit of the possible errors arising from the change in kinetic energy involved in the above variation of speeds was computed to be of the order of magnitude of 0.°004 C. Actually none was observable. For, in a run with the plug removed and with speeds of flow in the ratios 50 : 100 : 200 : 330 the bridge readings (with reference to an arbitrary zero) were 0.°037, 0.°038, 0.°038, 0.°038 respectively. The fastest flow exceeded the greatest speed of the air in the final runs. This run, moreover, was taken with the thermometer caps on, when the error from velocity cooling should be a maximum, as

is plain from a glance at Fig. 3. For, when the caps are removed, the speed of air past the thermometers would be less.

The formula used in this computation, namely,

$$c_p(T_1 - T_2) = \tfrac{1}{2}(w_2^2 - w_1^2) + g(h_2 - h_1)$$

was not strictly applicable, for, as in all deductions of this sort the temperatures could be given only by thermometers *moving with the gas*. Stationary thermometers would be expected to indicate smaller temperature differences. The preliminary experiments of Joule and Thomson, as well as those just outlined, are in agreement with this idea.

Aspirator Effect.—This is an effect cognate with velocity cooling. For to measure the pressure of a stream of fluid the manometer likewise should be moving with the fluid, strictly speaking. A test for error arising from this cause was made by taking readings on the differential manometer with the plug removed while the air was run through at velocities higher than those employed in the runs. The manometer showed zero reading throughout.

Effect of Varying Rates of Flow upon the Observed Temperature Drop.—These observations are depicted graphically in Fig. 4. Curve 2 was taken with the plug whose characteristic rate of flow has just been given,

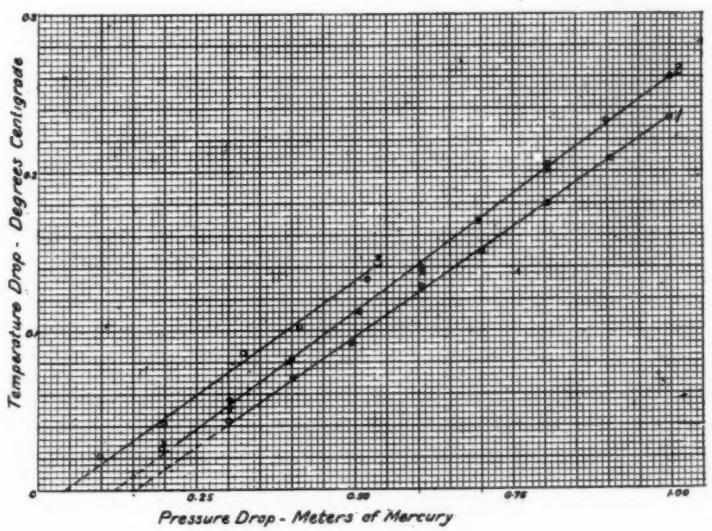

Fig. 4.

Preliminary Experiments, Varying Rate of Flow and Position of Guard Ring.

Curve 1: Relative Flow 0.7—Slope 0.28
" 2: " " 1.0— " 0.30
" 3: " " 3.0— " 0.29
Crosses: Guard Ring shifted 4 cm.—flow as in 2.

namely, 2.3 cm. per sec. per cm. of Hg pressure drop. Curve 1 applies to the same plug wrapped with rubber bands till its flow was 0.7 as great, while curve 3 is for a plaster of Paris plug whose flow was three times as great.

The first essential feature of these curves is that they are straight lines within the error of experiment, except near the origin. (This is true not only in the preliminary but in the final runs.) Near the origin the points were so irregularly distributed that they have been omitted from the diagram.

The second essential feature is that the more rapid the flow the nearer the curve approaches to a limiting line passing through the origin. A third feature to be noted is that these lines are sensibly parallel. These features will be taken up later, in discussing the effects of a residual heat leakage.

Heat Leakage by Conduction.—The nature of this residual heat leakage was sought in conduction, radiation and convection. Conduction through the gas does not seem probable. The only remaining path would be along the material of the plug. This point was tested by shifting

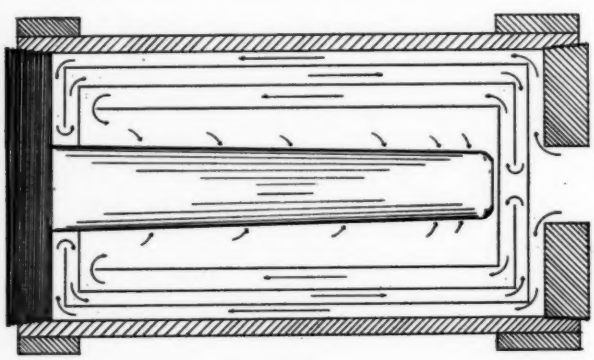

Fig. 5.

the guard-ring from a position 1.5 cm. from the plug flange *F* (Fig. 3) to a point 5.5 cm. therefrom. The results as shown by the rings and crosses (Fig. 4) rule out this source of error, the curves (No. 2) in these two cases being indistinguishable.

Heat Leakage by Radiation.—Since the surface of the plug must be at a different temperature (lower in case of air) from that of the walls of the plug casing, heat may pass by radiation across the annular space between them and thus reach the interior without first being absorbed by the gas itself, and so an error may be introduced. This was first tested by comparing runs with the dark iron casing walls lined with

bright tin and then without the tin. There was no systematic difference. Again a trial was made with three radiation shields on the one hand, disposed as in Fig. 5, in a large casing and on the other, with no radiation shields at all (the casing being that shown in Fig. 3). Fig. 6 shows that

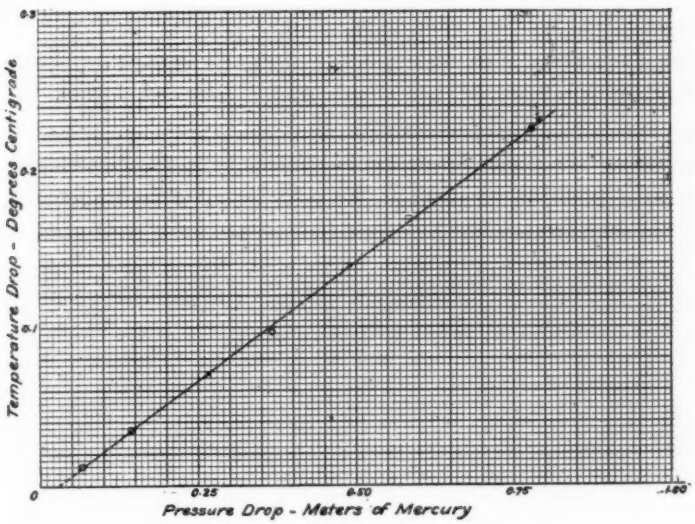

Fig. 6.

Preliminary Experiments, Effect of Radiation Shields.

Circles: No radiation shields
Crosses: 3 " "

these results also are indistinguishable. Radiation, then, is not to be looked for to explain the depression of these lines nor as a serious source of error.

Heat Leakage by Convection.—A turbulent motion of the gas surrounding the plug could possibly convey heat across from the walls of the casing without permanent absorption. If so, an increase in the inside diameter of the casing should reduce this error and shift the lines nearer to the origin. Now in the experiments of Fig. 6 (no shield), the annular space between the walls and the plug was about 6 mm. thick or about twice as thick as for the experiments of Fig. 4. The curve of Fig. 6 passes much nearer to the origin. Consequently convection must play a part.

It was not thought worth while to push these experiments further, the practical limit being apparently reached in the experiments of Fig. 6.

Influence of Density.—Where the mean density of the air is increased by operating at increased mean pressures, one should expect a minimizing effect upon the errors in the temperature readings, owing to the increased volumetric thermal capacity of the gas and the fact that the heat leakage

should not increase in the same ratio, if at all. This was verified by experimental runs, whose results are shown in Fig. 7, where it will be seen that curves corresponding to the higher pressures pass nearer the origin. Further confirmation in the final results were found and will be noted when these come up.

A second effect is observable here. The slopes of the lines fall off with increasing pressure. This again more properly comes up later, where the diminishing effect of increased mean pressure upon the Joule-Thomson coefficient is discussed.

Derivation of the Joule-Thomson Coefficient from the Observations.—We are now in a position to discuss the relation of μ to these preliminary data. It is seen from what has gone before, that the continual reduction

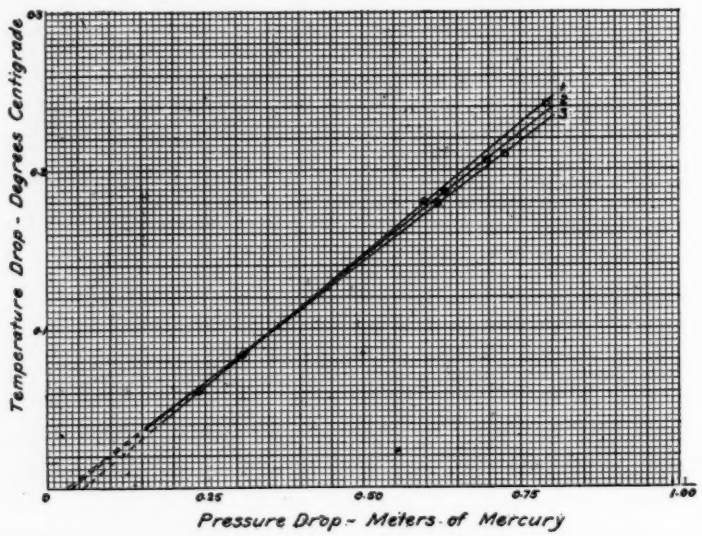

Fig. 7.

Preliminary Experiments, Varying Densities.

Curve 1: Mean pressure 2.5 meters mercury
" 2: " " 4.5 " "
" 3: " " 6.4 " "

of error by first reducing the heat-leak in obvious ways and secondly by increasing the mass of gas affected, has led in the main to the shifting of the curves of the type shown in Figs. 4, 6 and 7 so that their rectilinear portions (produced) are made to pass nearer to the origin without, however, changing their directions sensibly (exclusive, of course, of the pressure effect, which is entirely independent). The limiting ideal case, therefore, would be represented by a straight line passing through the origin, whose slope would be the true value of μ. The obvious step then

to take is to make the actual runs under conditions as nearly ideal as feasible; and for the values of μ adopt the values of the slopes of these straight lines without reference to their position. These values are taken to be as near the truth as the data are capable of yielding it.

The question may now be asked: Can anything be said as to the constancy of $u + pv$ or H along these plots? It will be remembered that after the gas has passed through the plug the increment in the function H is equal to the gain of heat per gram of gas during its passage. Now it is conceivable that the heat-leak (measured in calories per second) might be of such magnitude as to make the slope of the plots too steep for a locus of constant H, or again, such as to make it too flat.

Start, for example, with one of the smaller pressure drops and suppose there is a small heat leak. The resulting temperature drop will be too small. Let this observation be represented by a point on the (p, t) diagram, say, near the origin on a plot like that of Fig. 6. The value of H for this point will be greater than its value, H_0, for the origin, which represents the state of the gas on the high pressure side of the plug. A straight line, then, drawn from the origin to a point A, say, when there is a heat leak, will pass from regions of lower to regions of higher H and will be too flat. Now suppose that the experiment be carried to a higher pressure drop and a second point B is determined. As a different and an extreme case of heat-leak, let us suppose, for the moment, that from the point A onward it remains constant. Then, since the rate of flow has been increased, due to the increased pressure-drop after we leave A, the gain per gram falls off. The line AB, therefore, passes from higher to lower values of H and is too steep. Now let us try another hypothetical law for the heat-leak, namely, that from the point A onward, it is proportional to the rate of flow of gas. Then the gain in heat per gram remains fixed and the two points A and B are characterized by the same value of H. A line plotted under this condition would be, therefore, a line of constant H, although this value would be greater than H_0. In general, then, starting from the point A: if the heat-leak varies more rapidly than the first power of the rate of flow of gas, the plot is too flat; if, less rapidly, the plot is too steep. In call cases the plot will lie under the line $H_0 = \text{const.}$

The hypothesis that the heat-leak is proportional to the rate of flow of the gas seems a reasonable one to make for actual Joule-Thomson experiments, at least as a first approximation. For, as has been seen, the rate of flow is approximately proportional to the pressure-drop, which in turn is very closely proportional to the temperature-drop, and the latter again in turn would be expected to be proportional to the heat-leak,

certainly as far as conduction and radiation are concerned, and possibly convection too. In the case of convection, however, there seems to be a possibility that the leak would be speeded up in the case of turbulent motion and cut down in the case of stream-line motion, thus producing deviations from the proportionality relation on one side or the other. At present there is no way of deciding this point but the deviation in any case should be small.

If, then, the total heat-leak be small and if its deviation from being proportional to the rate of flow be likewise small, the deviations of our plots from true curves H = const. should be small to quantities of the second order of errors. It is hoped that this may be reasonably claimed for the final runs described in this paper.

In the light of what has just been developed, the actual plots are now susceptible of a further interpretation. The curve of Fig. 6, if completed by connecting up with the origin by the experimental determination of the requisite further points would of course curve upward in this region. This was actually done in some instances although some of the points were uncertain. This curvilinear portion of the plot, then, would represent a heat-leak varying more rapidly than a direct proportion of the flow-rate, while the remainder would represent a heat-leak proportional to this rate. Both the excess heat-leak and the uncertainty of the points near the origin are to be expected on account of the very slow, almost stagnant, flow of the air in experiments with such small pressure-drops.

As a matter of fact it is physically impossible for anything but an excess heat-leak to occur for this region. Otherwis we should have two curves, H and H_0 say, for which $H - H_0$ is finite, approaching intersection as a limit at an arbitrary point, namely, the origin of the diagram. We have, then, in other words, the surprising inference that it is impossible, in a throttling process, for a heat-leak to be continuously proportional to the rate of flow of gas below a finite limit of the flow and, likewise, of the pressure drop, although this would seem quite possible otherwise.

Referring now to Fig. 4, where the rate of flow of the air has been varied, other things being unchanged, by altering the porosity of the plug, the plots are explicable on the ground that the heat-leak is proportional to the rate of flow of the air in each case but that the constant of proportionality is smaller the greater the porosity of the plug.

Zeros of the Differential Thermometers.—In the determination of the slope of the lines just discussed, it is obviously unnecessary to know the precise value of the bridge setting when the pressure-drop is zero. This

knowledge was useful in the preliminary experiments in affording an index of the magnitude of the heat-leak. In the final run, therefore, the determinations of the zeros were discontinued. For they required time and at best were uncertain. The conditions for accuracy in a body of stagnant air in the pocket-like interior of the plug in the position shown in Fig. 3 are obviously unfavorable. The only way to put this accuracy on a par with the other readings would be to provide a way of opening the plug and sending a current of air through.

A matter well worth noting here is that, when this method of observation is employed, one is relieved of the necessity of a close adjustment to equality of the differential thermometers. The high side thermometer serves in reality merely as a sort of compensator for error due to fluctuations in the bath temperature, and an accurate knowledge of it even is unnecessary. For example the fundamental intervals of the two thermometers T_1 and T_2 differed by 0.3 per cent. Now suppose the temperature of the bath during a run changed by as much as 0.01 degree. Then the differential reading, after the steady state had been reached, would be changed by 0.00003 degree.

Values given for the Temperatures and Absolute Pressures.—In what follows μ will be discussed as a function of temperatures and pressures. The pressures will be the means of the pressures above and below the plug. On the diagram they will be represented by the mid-points of the limited straight lines there plotted. As to temperatures, the variations are too small to make it worth while to correct the bath temperatures.

Error from Moisture.—Tests made at a fixed temperature and pressure, in which the air from the room was passed through long-used calcium chloride first; then the drying material was omitted; finally fresh calcium chloride was put in. The values obtained for μ were 0.35, 0.34, and 0.33 degrees per meter respectively, showing a small increase due to moisture (and the poor quality of old calcium chloride). One should expect, then, that a final drying with phosphorus pentoxide would suffice. In the final runs this was used, with the exception of those at 30° C., and these, in spite of that, seem to fit well into the empirical formula derived from all the observations, as will appear later. The phosphorus pentoxide could be continually observed from the outside during the runs, and it was only at the ends of the longer ones that it had a gummy appearance.

Conduction of Heat along the Thermometer Leads.—After the final runs had been made, it was suspected that there might be an error arising from this cause. A new set of runs with the thermometer caps removed, exposing the thermometer wire to the stream of gas would test this point.

A number of observations were, therefore, made covering the same range of temperature and pressure. The galvanometer, of course, was quite unsteady under these conditions, but the agreement between the new and the old data was satisfactory. Thus the mean of ten runs with the caps off gave for μ a value 0.265 while the mean of ten runs at the same temperatures and pressures with the caps on gave 0.267 degrees C. per meter of mercury pressure-drop. This was well within the accidental error of the runs with caps off.

Regeneration Effect.—After the experiments described in this paper had been completed, the paper by Trueblood, referred to in the beginning, appeared, in which is described a form of heat-leak arising from the peculiar geometry of the radial flow apparatus. The nature of this regeneration effect can best be described by quoting from Trueblood's paper: "At its open end, the plug is necessarily brought, for purposes of mechanical support, into good thermal contact with the metal walls of the case. As a result, fluid which has passed the low side thermometer is provided with a thermally short path of communication with fluid which has not yet passed through the plug. This results in a depression of the temperature of the latter, which, joining the low side fluid at at a temperature therefore lower than then exists there, contributes to a still further depression of the temperature of the fluid which has not yet passed. This cumulative action, similar in principle to that taking place in certain types of liquid air machines, is limited by the ability of the bath to supply heat to the low side fluid. . . . The effect of the action just described on the observed temperature drop is indirect, since the fluid directly affected does not pass the low side thermometer. But the temperature depression produced in the neighborhood of the open end produces indirectly, by conduction through the walls of the plug, the walls of the case, the inside lagging and, doubtless, to some extent through the fluid itself, a depression of the temperature of fluid which does pass the low side thermometer; that is, there is an outward leak of heat from fluid between thermometers to fluid which has passed the low side thermometer with the result that the observed temperature drop is too high."

In the author's apparatus the regeneration effect, he believes, was negligible, although, as a matter of fact, its possibility was not foreseen. For, under the heading *heat leakage by conduction*, it was shown that a shift in position of the guard ring did not lead to a change in reading. Now since the temperature depression of the low side gas is due to the "regeneration" process should be manifest in greater and greater degree at points nearer and nearer to the mechanical support, it should have been shown up by the test in question, which, as has just been seen, was not

the case. This result may have been due to the unusually long and narrow proportions of the plug used. A natural remedy for the regeneration effect or any effect arising from conduction would seem to be the employment of a long plug.

Final Results.

Between August, 1915, and January, 1916, fourteen determinations of the Joule-Thomson coefficient (μ) were made at five temperatures between 0° C. and 100° C. and at mean pressures of 2.5, 4.5 and 6.4 meters of mercury.

In Table I. are collected the data summarized from each run. The first four columns need no comment. The "bridge readings" of column 5 correspond to the temperature-drop, without being reduced to degrees.

Table I.

1. Date.	2. Bath Temp.	3. Pressure (Meters).	4. Pressure Drop (Meters).	5. Bridge Readings.	6. Slope (Bridge Units per Meter).	Residuals. 7. Bridge Units.	Residuals. 8. Degrees.	9. Wt.	10. Intercepts (Bridge Units).
1916									
Jan. 10	15°.9	2.45	.763	14.26	0.698	—	—	0.2	
			.260	10.75					
" "		6.50	.694	13.53	0.622	—	—	0.3	
			.263	10.85					
1915									
Aug. 20	30°.0	2.49	.792	4.67	0.635	−0.01	−0.0005	1.0	−0.34
			.599	3.48		+0.02	+0.001		
			.311	1.63		0.00	.0000		
			.241	1.18		−0.01	−0.0005		
" 23	"	4.48	.697	3.98	0.607	−0.01	−0.0005	1.0	−0.24
			.631	3.59		0.00	0.0000		
			.298	1.60		+0.03	+0.0015		
			.199	0.94		−0.03	−0.0015		
" 26	"	6.40	.726	4.07	0.588	−0.01	−0.0005	1.0	−0.19
			.620	3.46		−0.02	−0.001		
			.310	1.63		0.00	0.0000		
			.255	1.32		0.01	+0.0005		
Nov. 24	50°.0	2.50	.747	4.12	0.560	+0.02	+0.001	1.0	−0.08
			.653	3.54		−0.03	−0.0015		
			.343	1.84		+0.01	+0.0005		
			.264	1.39		0.00	0.0000		
Nov. 29	"	4.50	.820	4.37	0.535	−0.05	−0.0025	0.5	+0.03
			.689	3.77		+0.05	+0.0025		
			.309	1.71		+0.03	+0.0015		
			.193	1.03		−0.03	−0.0015		
Dec. 1	"	6.33	.790	4.28	0.529	−0.02	−0.001	1.0	+0.12
			.711	3.90		+0.02	+0.001		
			.307	1.74		0.00	0.0000		
			.193	1.14		+0.01	+0.0005		

TABLE I. (*Continued*).

1. Date.	2. Bath Temp.	3. Pressure (Meters).	4. Pressure Drop (Meters).	5. Bridge Readings.	6. Slope (Bridge Units per Meter).	Residuals. 7. Bridge Units.	Residuals. 8. Degrees.	9. Wt.	10. Intercepts (Bridge Units).
1915									
Dec. 6	70°.0	2.53	.769	3.93	0.496	+0.02	+0.001	1.0	+0.1
			.500	2.54		−0.04	−0.002		
			.259	1.41		+0.02	+0.001		
Dec. 8	"	4.36	.747	3.84	0.480	−0.01	−0.0005	1.0	+0.26
			.497	2.66		+0.01	+0.0005		
			.247	1.44		−0.01	−0.0005		
Dec. 13	"	6.40	.718	3.72	0.468	0.00	0.0000	1.0	+0.36
			.498	2.70		+0.01	+0.0005		
			.255	1.55		0.00	0.0000		
Dec. 16	90°.0	2.44	.746	4.87	0.441	0.00	0.0000	1.0	+1.57
			.509	3.83		0.00	0.0000		
			.257	2.71		0.00	0.0000		
" "	"	4.52	.747	4.91	0.421	−0.01	−0.0005	1.0	+1.78
			.495	3.88		+0.02	+0.001		
			.248	2.81		−0.01	−0.0005		
Dec. 15	"	6.35	.743	3.51	0.406	−0.02	−0.001	1.0	+0.51
			.506	2.60		+0.04	+0.002		
			.253	1.52		−0.02	−0.001		

This reduction is more simply done later. Column 6 gives the slope of the straight line that would be formed by plotting after the manner of Figs. 6 and 7, but actually they have been calculated by the method of least squares. The residuals in temperature, shown in column 8, give no evidence of a systematic deviation from the straight line and, moreover, the order of their magnitude is seldom over 0°.001 C. The weights (column 9) assigned to the several runs are the same for all except three, where experimental difficulties of a temporary sort turned up during the respective runs. In the two runs of January 10 it was impractical to get more than two points for each straight line, so there was no least square reduction. That carried out on November 29 suffered from a derangement of the pressure controlling apparatus. The later runs included one less point each but the gain in observing experience about balanced the omission of one point, and so the weights for these were kept at unity. The "intercepts" (column 10) on the temperature axis, are known to within additive constants only, except for the runs at 30° C., where zero readings of the differential thermometers were taken. The only purpose these data serve here is to furnish further evidence for the conclusions stated under the head "*influence of density*." It will be seen that with ascending pressures, hence increasing densities, the intercepts progressively rise along the temperature axis, with one exception.

The Joule-Thomson Coefficient Expressed as a Function of Temperature and Pressure.—The values of the slopes (column 6) reduced to the proper units are taken as the values of μ for reasons already given. This reduction is now made by the use of the multiplying factor 0.5178 together with formula (8). μ is then expressed in degrees C., hydrogen scale, temperature-drop per meter of mercury pressure-drop.

The fourteen values of μ thus obtained are classified in Table II.

TABLE II.

Approximate Pressure. (Meters.)	15° C.	30° C.	50° C.	70° C.	90° C.
	.358	.327	.290	.258	.232
2.50	(+.008)	(+.002)	(−.002)	(−.002)	(+.002)
	(+.002)	(+.001)	(.000)	(−.001)	(+.001)
		.312	.277	.250	.220
4.50		(−.001)	(.000)	(−.001)	(−.001)
		(−.002)	(−.002)	(.000)	(−.002)
	.319	.302	.274	.244	.213
6.40	(−.006)	(.000)	(+.002)	(+.002)	(−.001)
	(−.010)	(.000)	(+.004)	(+.003)	(−.002)

Upper line of residuals—five-constant formula.
Lower line of residuals—three-constant formula.

according to temperature and pressure. To these values were fitted, by least square computation, two empirical formulas, one a five-constant formula in t, the other a three-constant formula in $t + 273$ or τ. In the same table are included in parentheses, under each observed value of μ, the residuals (obs.-calc.) obtained with each of these formulas, the upper one applying to the former, the lower, to the latter formula.

The five-constant formula was tried following upon an initial inspection of the observations, which showed that the variations of μ were linear in p but not linear in t. Consequently a second degree term in t was included. The formula is

$$\mu = + 0.3935 - 0.00691p - 0.001835t + 0.00000134t^2 + 0.0000325pt, \quad (9)$$

the units being as above specified.

Five constants make an unwieldy formula and seemed quite too many for the limited range of temperatures and pressures here employed. Resort was then had to the three-constant formula (4) suggested by the use of the equation of van der Waals. The least square reduction for this gave

$$\mu = - 0.2599 + 181.96\frac{1}{\tau} - 552.4\frac{p}{\tau^2}, \quad (10)$$

where $\tau = 273 + t$. This formula is plotted in Fig. 8, which shows likewise the observed points.

The five-constant formula agrees a trifle more closely with the observations than does the other, as should be expected, having two more constants, but there is little to choose between them in this respect. All things considered, the three-constant formula is to be preferred; it is more rational and is simpler.

The computations of these formulæ were subjected to the standard

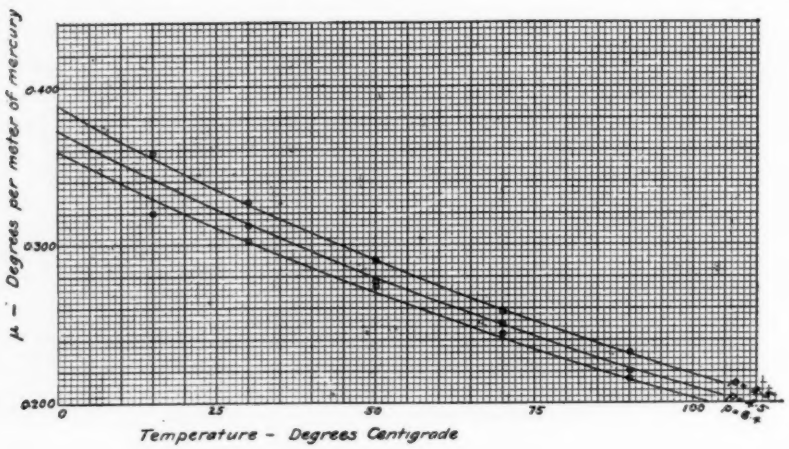

Fig. 8.

Joule-Thomson Coefficient, as a Function of Temperature and Pressure.

Curves are graphs of the formula:

$$\mu = -0.2599 + 181.96\frac{1}{\tau} - 552.42\frac{p}{\tau^2}$$

Circles are observed values.

numerical checks throughout. The smallness of the residuals, being on the whole less than one per cent. would indicate, at least for the present observations, that a better formula is not worth looking for.

Comparison with Other Results.—Joule and Thomson gave as their formula for air

$$\mu = 0.92\left(\frac{273.7}{T}\right)^2 \text{degrees C. per 100 inches of mercury,}$$

which, by reduction, is

$$\mu = 0.362\left(\frac{273.7}{T}\right)^2 \text{degree C. per meter of mercury.}$$

Their data have been embodied by Rose-Innes (*loc. cit.*) in the formula

$$\mu = -0.275 + 178\frac{1}{T} \text{ reduced to degs. C. per meter of mercury,}$$

which resembles (10) omitting the pressure term. The observations of Joule and Thomson, it will be remembered, did not indicate an effect of pressure.

Buckingham, by making use of the results of Kester on carbon dioxide and of Joule and Thomson on oxygen, air, nitrogen, and hydrogen, applied the law of corresponding states and found two formulas of similar type, one of which is

$$\mu = \frac{a_1}{\tau - b_1} - d_1, \qquad \tau = 273 + t.$$

A few numerical values calculated by the aid of this formula and the values given for the constants, will be found further on in Table III.

The only experiments published showing a pressure effect for air are those of Vogel and of Noell. The latter, being performed subsequently in the same laboratory may be considered as superseding the former. However, it is well to state Vogel's formula, namely,

$$\mu = 0.268 - 0.00086p \quad \text{(pressures in kg. per cm}^2\text{)},$$

which holds for the fixed temperature only.

The lengthy formula of Noell is quoted near the beginning of this paper. The pressure coefficient at 10° C. is practically the same in both cases. At 0° C. Noell's pressure coefficient is -0.0015 while that found by the author is -0.0074 the units in both figures being degrees C. and meters of mercury. The agreement here leaves something to be desired but it is well to note that the greater portion of the data to which Noell's formula was adjusted lay in a range of much higher temperatures and pressures than the temperatures and pressures of the present paper. It is interesting to note that Noell's formula is also linear in p and that both coefficients are negative.

Further corroborative evidence as to the negative sign may be found in the calculations of Dalton (*loc. cit.*) for hydrogen based on the empirical equations of state of Kamerlingh-Onnes. He plots numerous curves of the integrated Joule-Thomson effect, or in other words curves H = const. over a wide range in temperature and pressure, *i. e.*, from 1 to 100 atm. and $-215°$ C. to $+17°$ C. These curves in the (p, t) plane were all concave downward, showing a negative pressure coefficient of μ for hydrogen, over the whole field, which covered some inversion points and both positive and negative values of μ. One would expect that an application of the law of corresponding states might lead to the same thing for all gases, although a general statement of this sort could not be made. In fact, accepting van der Waals' equation for the moment, a

glance at equation (3) shows that the sign of the expression

$$\left(6b - \frac{4a}{RT}\right)$$

determines the sign of the pressure coefficient. In regard to carbon dioxide, Natanson found a positive coefficient, and Kester found no dependence upon pressure except at 26.4 atm. and here an increase in μ over its value at lower pressures was indicated. The matter on the whole for carbon dioxide seems undecided.

In Table III. are set forth for comparison a few numerical values for μ calculated from the formulæ of other observers above quoted (omitting those of Vogel and Rose-Innes). In general the values of the present paper exceed the other values. The former, at 4.5 meters pressure are in closest agreement with those of Buckingham. It is of interest to note, however, that, choosing a temperature of 0° C. for example, the integrated cooling effect over a drop of about 7 atmospheres calculated by the author's formula agrees with that set down for "corresponding states." This was roughly the pressure-drop in the experiments of Joule and Thomson.

TABLE III.

t° C.	Joule and Thomson.	Corresponding States. (Buckingham.)	Noell $p = 1m.$	Present Paper.		
				$p = 1m.$	$p = 4.5m.$	$p = 6.4m.$
0	.362	.374	.365	.399	.373	.359
50	.259	.270	.244	.298	.278	.270
100	.194	.212	.165	.224	.210	.203

Calculation of the Temperature of the Ice Point on the Thermodynamic Scale.—The general relations are

$$\frac{v_{100}}{T_{100}} - \frac{v}{T_0} = \int_{T_0}^{T_{100}} \frac{\mu c_p}{T^2} dT \quad \text{(pressure = const.)}, \qquad (11)$$

$$v_{100} = v_0(1 + 100\,\alpha),$$

$$T_{100} - T_0 = 100.$$

The first of these is one of the two ways of integrating equation (2); the second equation defines, in terms of experiment, the mean temperature coefficient at constant pressure of the gas used in the experiment; while the last is a mathematical definition. The limits of integration are the two temperatures of the ice point and the steam point.

If we factor out a mean value of c_p (which varies but slightly within these limits) calling it $\overline{C}_p$ and call the value of the remaining definite integral $(I_{100} - I_0)$, noting that $1/v_0 = \rho_0$ the density of the gas at the

given constant pressure and at the ice point, then the combination of these three relations results in

$$T_0 = \frac{1}{\alpha} + \frac{T_0(T_0 + 100)}{100\alpha} \rho_0 \bar{C}_p (I_{100} - I_0)$$

without approximation.

The first term on the right is the temperature of the ice point on the scale of the gas in question. The second term is the quantity that must be added thereto in order to derive the same temperature on the thermodynamic scale. It is small and may be called a "correction." Its relative magnitude will be seen to come out only about 0.0037 times the first term.

Now the accuracy of this term is limited by that of the determinations of μ, namely an order somewhat under one per cent. Expressed in degrees this would come to about 0°.01 C. The following two approximations therefore are permissible: First, T_0 may be replaced by 273; secondly, the evaluation of the integral

$$\int_{T_0}^{T_{100}} \frac{\mu}{T^2} dT,$$

in which formula (9) or formula (10) must be used, t may be treated as if it were $T - 273$ in formula (9) and in formula (10) τ may be treated as if it were T. Further, or successive approximations are unnecessary. The above formula, with these approximations, then becomes

$$T_0 = \frac{1}{\alpha} + \frac{273 \times 373}{100\alpha} \rho_0 \bar{C}_p (I_{100} - I_0). \qquad (12)$$

The value of $(I_{100} - I_0)$ has been computed and found to be

$+ 0.000306$ by (10), the three-constant formula for μ,

and

$+ 0.000308$ by (9), the five-constant formula for μ,

the unit of pressure still being one meter of mercury at 0° C. in this locality.

The expression of this result in terms of absolute units and the calculation of the remainder of the formula were carried out by means of the following data:

density of mercury $= 13.595$ gm. per cm^3,

$g = 980$ cm. per sec^2,

$\bar{C}_p = 241$ cal per gm. per deg.,

1 cal. $= 4.187 \times 10^7$ ergs.

$\rho_0 = 0.001293 \frac{100}{76}$ gm. per cm^3,

$\alpha = 0.00367282$.

The value for g is rounded off from 979.937, the figure given as determined in this locality by the U. S. C. and G.S.; that for $\bar{C}_p$ is a mean taken from the papers of Swann and Scheel and Heuse already mentioned. The value for α was determined with great care and precision by Chappuis[37] at the standard thermometric pressure of one meter of mercury. The reciprocal of this is 272.270.

The correction term in (12) obtained by use of these data are

1.093 by the three-constant formula

and

1.100 by the five-constant formula,

whence, for the thermodynamic temperature of melting ice, we get

$T_0 = 273°.36$ by the three-constant formula

and

$T_0 = 273°.37$ by the five-constant formula.

The other most recent calculations are by Buckingham (1908) using the Joule-Thomson coefficient for various gases adjusted into a single reduced formula by the "law of corresponding states," and by Berthelot (1907) using the characteristic equation. Previously in 1903, he had computed values on the basis of the Joule-Thomson effect. These results are collected in Table IV.

TABLE IV.

Author.	T_0.	Gas.	Method.	Reference Used Here.
Buckingham (1908)	273 273	Air	J-T effect	Buckingham[31] (1908)
	273.286	N_2	"	"
	273.049	H_2	"	"
	273.267	CO_2	"	"
Berthelot (1903)	273.13	H_2	"	Buckingham[31] (1907)
		N_2		
		CO_2		
		Air		
Bertholet (1907)	273.04	H_2 in Pt-Ir (1)	Characteristic equation	Berthelot[32] (1907)
	273.07	" " " (2)		
	273.10	" in *verre dur*		
	273.09	N_2		

The value arrived at in this paper is higher than any of these; and, further, it will be noted that the method by the Joule-Thomson effect gives higher values than does the method using the characteristic equation of the gas. This fact has been noted by Buckingham and others but has not been considered to be satisfactorily explained. Rose-Innes and Berthelot (the latter while discussing his values obtained from hydrogen)

have suggested the possibility of a surface action at the walls of the containing bulb, such as the formation of a layer of gas whose density is different from that to be found in the interior. This, of course, affects the main term $1/\alpha$.

Pressure Coefficient of α.—A partial comparison may be made here by taking into consideration the pressure coefficient of α found by Chappuis[37] for nitrogen and that deducible for air from the results of this paper. Reference to equation (12) will show that the correction term is proportional to the density ρ_0 (neglecting the pressure effect in μ, an influence of the second order) and hence proportional to the pressure, which, in the present units, has the value 1. T_0, being a constant, this term is, therefore, the pressure coefficient of the reciprocal of α. The pressure coefficient for α, then, is computed to be 0.0000147 for air, while Chappuis finds the value 0.0000119 for nitrogen, or about four fifths as much, an agreement which, at least, is qualitative.

Correction to the Constant-pressure Air Thermometer between the Ice and Steam Points.—Here, since by definition, the centigrade gas and centigrade thermodynamic scales must agree at both end-points, a closer agreement among the results from various sources is to be expected.

We have, as before, the general relations

$$\frac{v}{T} - \frac{v_0}{T_0} = \int_{T_0}^{T} \frac{\mu c_p}{T^2} dT \equiv \bar{c}_p(I - I_0)$$

and

$$v = v_0(1 + \alpha t),$$

defining t on the gas scale in question.

Now let

$$T - T_0 = t_a$$

defining t_a on the thermodynamic scale and

$$T_0 = \frac{1}{\alpha} + \eta$$

where η stands for the correction term in (12).

Therefore, since $v_0 = 1/\rho_0$,

$$T_0(1 + \alpha t) - T = TT_0\rho_0\bar{c}_p(I - I_0).$$

The left-hand member becomes

$$-t_a + T_0\alpha t = -t_a + t + \alpha\eta t.$$

Therefore the formula at once reduces to

$$t_a - t = \alpha\eta t - TT_0\rho_0\bar{c}_p(I - I_0),$$

in which $t_a - t$ is the correction sought.

Replacing η now by its expression in (12) and noting that, for the same reasons as before it is permissible, in the right-hand member, to identify t with t_a, c_p with C_p, and to replace T_0 and $1/\alpha$ by 273, the equation finally becomes

$$t_a - t = 273\rho_0\bar{c}_p\{3{\cdot}73(I_{100} - I_0)t - (I - I_0)(t + 273)\}, \qquad (13)$$

which, inspection shows, vanishes at both the ice and steam points, as, of course, it should. The values of $\bar{C}_p$ and ρ_0 are the same as those given for the computation of (12). $\bar{C}_p$ and $\bar{c}_p$, strictly speaking, are not identical, owing to the differing limits of their respective integrals, but it is obvious that their difference is not sufficient to affect the computations.

Corrections $(t_a - t)$ calculated by this formula for every 10° C. are to be found in the last column of Table V. The other columns are copied from Buckingham's article in the Phil. Mag., 1908.[31] The corrections are negative, that is, the numbers in the table are to be subtracted from the constant-pressure readings. The new values and those of Berthelot in this instance are seen to be practically identical. Chappius (*loc. cit.*), moreover, states that the air and nitrogen scales are sensibly the same in this interval; so that we have here a real basis for comparison. This is agreement within the accuracy of gas thermometry.

TABLE V.

Thermodynamic Corrections to the Constant Pressure Nitrogen Scale Obtained by Various Writers, Compared with the Corrections to the Constant Pressure Air Scale Deduced from the Joule-Thomson Effect. 1,000 mm. = pressure.

t°C.	Rose-Innes, 1901.	Callendar, 1903.	Berthelot, 1903.	Buckingham, 1907.	Mean.	This Paper (Air), 1916.
10	0.0120	0.0109	0.010	0.0078	0.010	0.0100
20	0.0205	0.0188	0.017	0.0137	0.017	0.0170
30	0.0261	0.0236	0.022	0.0179	0.022	0.0212
40	0.0288	0.0260	0.024	0.0203	0.025	0.0235
50	0.0289	0.0260	0.024	0.0209	0.025	0.0238
60	0.0269	0.0240	0.022	0.0198	0.023	0.0218
70	0.0228	0.0204	0.019	0.0172	0.020	0.0189
80	0.0168	0.0151	0.014	0.0129	0.015	0.0141
90	0.0092	0.0081	0.007	0.0071	0.008	0.0068

Variation of c_p with Pressure.—Recent work of Holborn and Jacob[38] on c_p for air at 60° C. and at pressures from 1 to 200 atmospheres affords a further comparison of the present work with that of other observers in that the Joule-Thomson effect can be utilized to evaluate the pressure coefficient of c_p.

Writing equation (2) in the form

$$\mu c_p = T\left(\frac{\partial v}{\partial T}\right)_p - v$$

and differentiating with respect to T at constant p, we get

$$\mu\left(\frac{\partial c_p}{\partial T}\right)_p + c_p\left(\frac{\partial \mu}{\partial T}\right)_p = T\left(\frac{\partial^2 v}{\partial T^2}\right)_p = -\left(\frac{\partial c_p}{\partial p}\right)_T, \qquad (14)$$

the last member following directly from a well-known equation in thermodynamics.

Now the left-hand member can be evaluated by using either formula (9) or (10) for μ and (say) Swann's values (*loc. cit.*) of c_p and $(\partial c_p/\partial T)_p$. It should be noted that, in regard to units, c_p may be expressed in calories per gm. per deg., since the equation is homogeneous in that physical quantity. Also since μ is here expressed in degrees per meter of mercury and since the data of Holborn and Jacob for $(\partial c_p/\partial p)_T$ are expressed in atmospheres for the pressure unit, the left hand member must be multiplied by 0.76 to make the two sets of results comparable. Finally T must be put equal to $273 + 60 = 333$, the temperature of Holborn and Jacobs' experiments.

Now Swann gives at one atmosphere,

$$c_p = 0.241 \quad \text{and} \quad \left(\frac{\partial c_p}{\partial T}\right)_p = 0.000016,$$

then by the 3-constant formula (10) also at 1 atmosphere

$$\mu\left(\frac{\partial c_p}{\partial T}\right)_p = 0.0000047,$$

$$\text{and} \quad c_p\left(\frac{\partial \mu}{\partial T}\right)_p = -0.0003901.$$

The sum of these two (of which the first is almost negligible) is -0.0003854. Multiplying by 0.76 we get

$$\left(\frac{\partial c_p}{\partial p}\right)_T = 0.000293 \text{ cal. per gm. per deg. per atm.}$$

The value of this quantity from Holborn and Jacobs' empirical interpolation formula, namely,

$$10^4 c_p = 2413 + 2.86p + 0.0005p^2 - 0.00001p^3,$$

is

0.000286 cal. per gm. per deg. per atm.

and from their observations at their lowest range of pressures alone (namely 1 to 25 atmospheres) it is

0.000312 cal. per gm. per deg. per atm.

The agreement here is about as good as would be expected. Moreover it is corroborative as regards a comparison between two widely different forms of continuous flow experiments.

Acknowledgments.—My thanks are due to Professor Ames, who suggested the work, for his encouragement and continual interest throughout its course; to my associate Professor C. M. Sparrow, for aid in making computations, and for valuable criticisms and suggestions, and to my colleague Professor Mitchell for aid in the least square reductions. In addition I have gained valuable information on experimental matters from the Bureau of Standards, particularly from Messrs. H. C. Dickinson and N. S. Osborne. For mechanical work I am indebted to Messrs. A. W. Barlow, I. J. Shepherd and M. M. Fitzhugh, students, who at various times have constructed parts of the apparatus.

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UNIVERSITY OF VIRGINIA,
January, 1919.

ERRATA.

Vol. XIII., April, 1919, in the article by A. F. Kovarik, entitled "The Automatic Registration of α-particles, β-particles and γ-ray and X-ray Pulses," page 277, second line from bottom, the first P_2 should read P_1; page 278, line 28, 4.77×10^{-11} should read 4.77×10^{-10}; page 280, line 32, first word "or" should read "for."

Vol. XIII., April, 1919, in the abstract by Irwin G. Priest, entitled "A New Formula for the Spectral Distribution of Energy from a Complete Radiator," in equations (2) and (3), pages 314 and 316, $A - \frac{1}{3}$ should read $A^{-1/3}$; line 6, page 317, "are" should read "an"; line 10, page 317, D^2 should read D_2.

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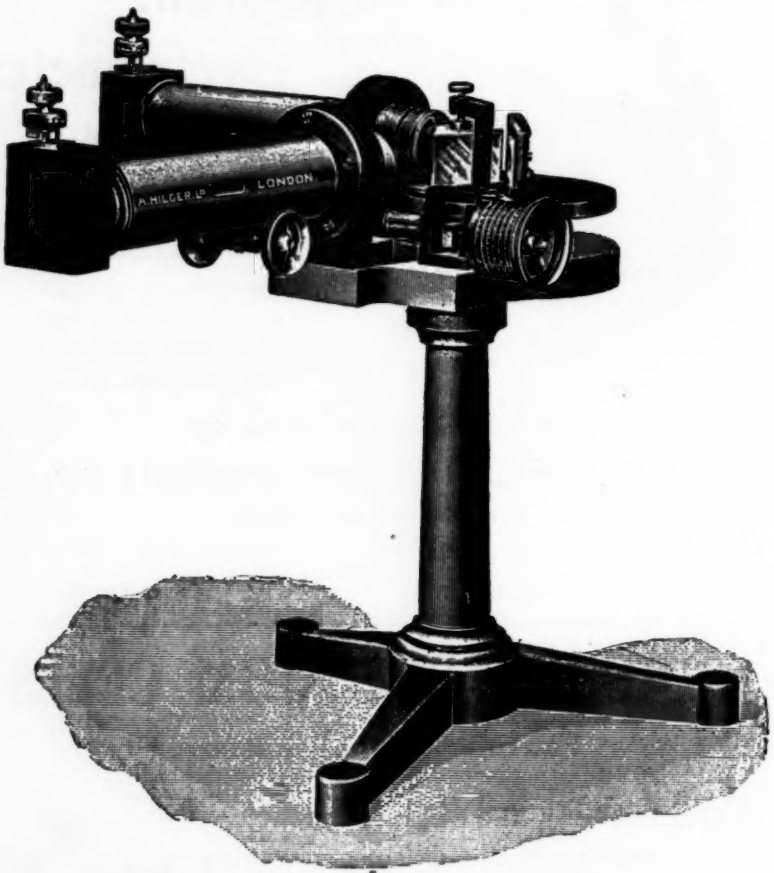

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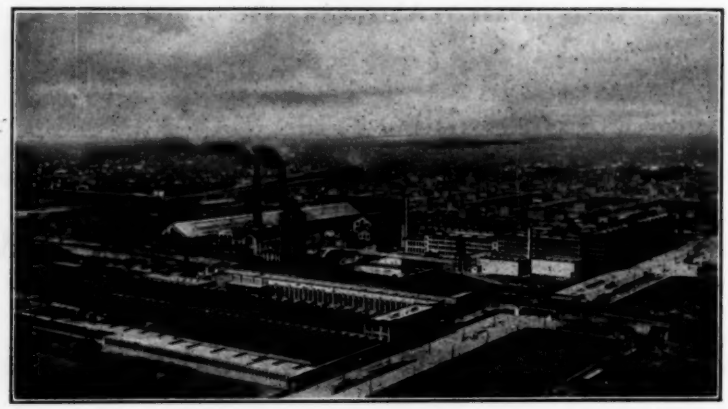

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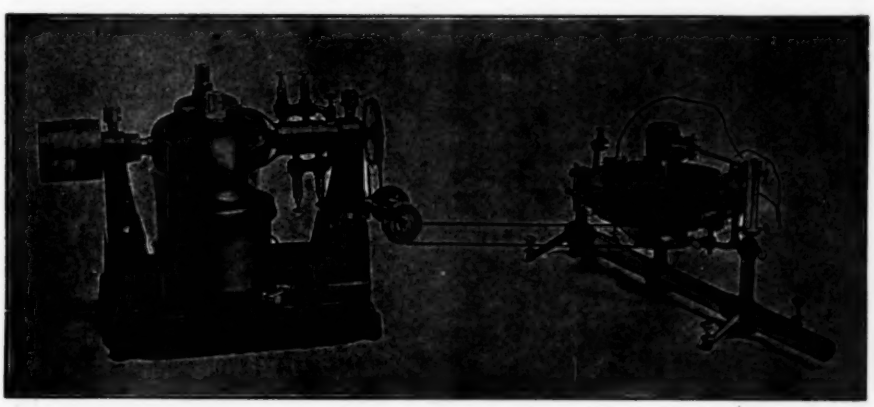

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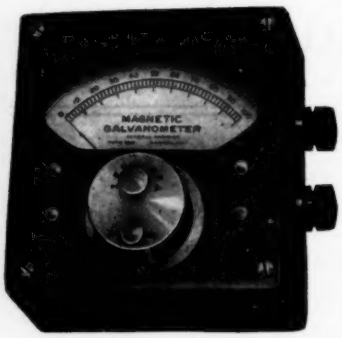

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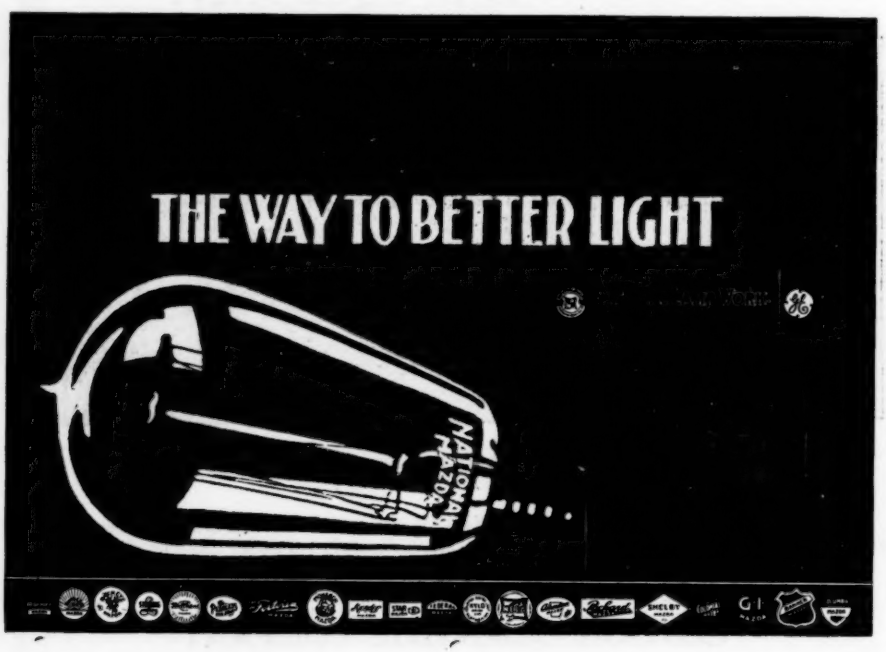

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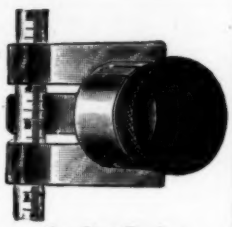

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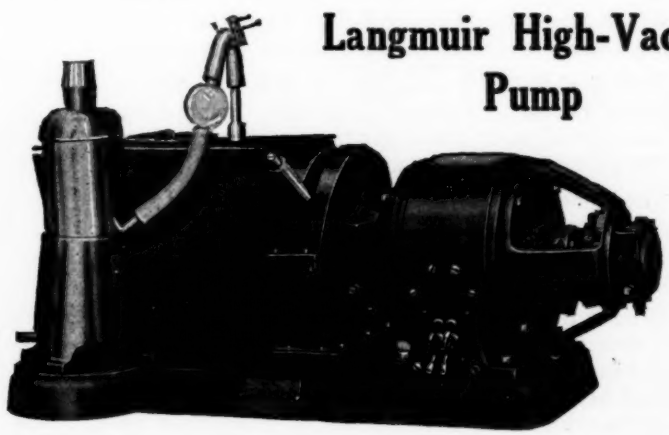

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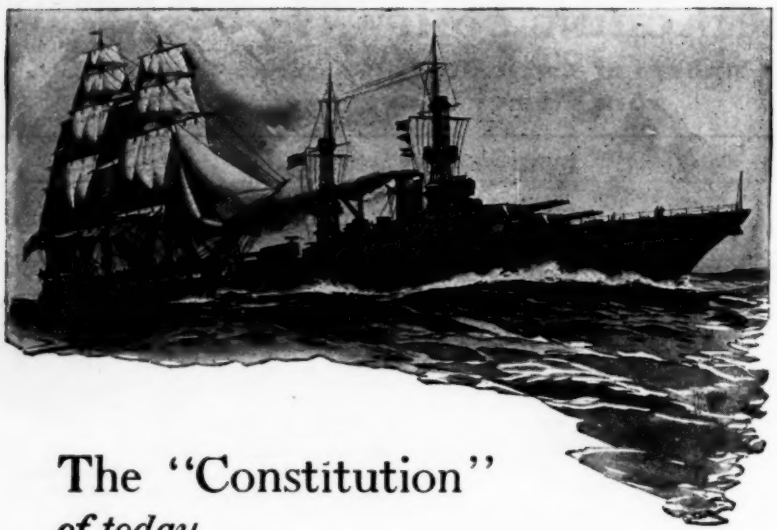

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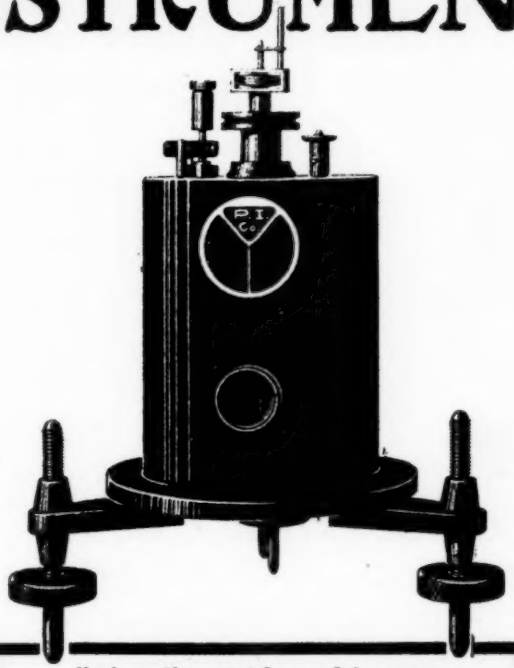

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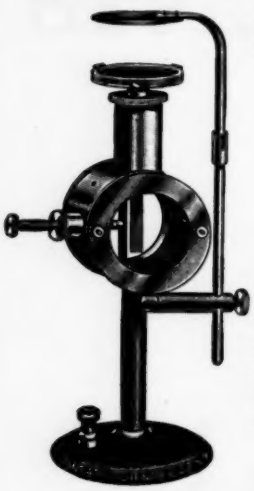

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